EVALUATING THE REMOVAL EFFICIENCY OF SEWAGE SLUDGE-DERIVED ACTIVATED CARBON FOR METHYL-TERT BUTYL ETHER-CONTAMINATED WATER.

BY

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To Allah and then to my mother and father

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LISTS OF ABBREVIATIONS

SDAC	Sewage Sludge Derived Activated Carbon
SBAs	Sludge – Based Adsorbents
CAC	Commercial Activated Carbon
AC	Activated Carbon
GY	Gac Yield
MTBE	Methyl-tert-Butyl-Ether
USEPA	United State's Environmental Protection Agency
3K-700-30	Adsorbent produced using KOH(aq): Sludge mixing ratio of 3:1 at 700 ^{0}C with a dwell time of 30mins
2Z-700-90	Adsorbent produced using $ZnCl_2$(aq): Sludge mixing ratio of 2:1 at 700 ^{0}C with a dwell time of 90mins
2K-500-90	Adsorbent produced using KOH(aq): Sludge mixing ratio of 2:1 at 500 ^{0}C with a dwell time of 90mins
2Z-500-30	Adsorbent produced using $ZnCl_2$(aq): Sludge mixing ratio of 2:1 at 500 ^{0}C with a dwell time of 30mins
PYR	Pyrolyzed form of 2Z-700-90
BET	Brunauer-Emmett-Teller
TGA	Thermogravimetry Analysis
DSC	Differential Scanning Calorimetry
SEM	Scanning Electron Microscopy
FESEM	Field Emission Scanning Electron Microscopy
EDX	Energy Dispersive X-ray
FTIR	Fourier Transformed Infrared
AOPs	Advanced Oxidation Processes
DOE	Design of Experiment

ABSTRACT

In this study, sewage sludge derived activated carbon (SDAC) was synthesized, characterized and assessed for its Methyl Tert-Butyl Ether (MTBE) removal efficiencies in a contaminated aqueous solution. The sludge was chemically activated with zinc chloride and pyrolyzed afterwards to produce SDAC. Four selected adsorbent materials were then characterized using the BET, Thermogravimetry (TG), SEM-EDX and FTIR techniques. The results of the analyses showed that the respective surface area values of 3K-700-30, 2Z-700-90, 2K-500-90, and 2Z-500-30 upon acid washing were 451 m^2/g, 385 m^2/g, 53 m^2/g and 38 m^2/g. The SEM-EDX analyses suggested the minerals (i.e. Fe, Al, Mg, Mn, Ca and Na) and biological components (Cocci, bacilli, spirilla, and vibrio) of the raw sludge were removed by the higher pyrolytic temperature and acid-water washing procedures. FTIR suggests hydroxyl group, carboxylates and aliphatic $–CH_3$ as the probable interplaying functional groups of the adsorbent. Adsorbent 2Z-700-90 was eventually selected based on its superceding qualities (yield of 70%, premium thermal ability of 50% and BET surface area of 385 m^2/g) for its capacity to remove MTBE. The adsorbent 2Z-700-90's MTBE removal efficiency of 70% was achieved at optimum conditions of pH 6, agitation speed of 150rpm, 60 minutes of contact time, 2g/L dose of adsorbent and initial MTBE concentration of 1ppm. The adsorption behavior of SDAC fitted better into pseudo-second-order reactions. This work demonstrated a beneficial use of a sewage sludge for water treatment

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ملخص الرسالة

في هذه الدراسة، تم تصنيع الكربون المنشط من حمأة مياه الصرف الصحي ومن ثم تصنيفه وتقييم كفاءته في إزالة إيثر ثلاثي ميثيل البيوتيل من محلول مائي ملوث. تم تنشيط الحمأة كيميائيا مع كلوريد الزنك و بعد ذلك نشطت بايروليزد لإنتاج الكربون المنشط المنتج من حمأة مياه الصرف الصحي باستخدام أحد الطرق المستخدمة في تصميم التجارب تعرف ب تصميم الفاكتوريال. تم في نهاية المطاف تحسين أربعة مواد من الممتزات وصنفت باستخدام طريقة (BET) وطريقة ثيرموغرافيمتري (TGA) وطريقة المسح الضوئي بالمجهر الإلكتروني إلى جانب تشتيت طاقة الأشعة السينية الطيفي (SEM) وجهاز "فوريه" لتحويل طيف الأشعة تحت الحمراء (FTIR). كشفت نتائج التحاليل أن قيم BET تساوي 451 متر مربع / جم و 385 متر مربع / جم و 53 متر مربع / جرام و 38 متر مربع / جرام تم تحقيقها على التوالي ل 3K-700-30، 2Z-700-90، 2K-500- 90، و 2Z-500-30 بعد غسل بالحمض. كشفت التحاليل (SEM/EDX) أن المعادن (الحديد، الألمنيوم، المغنيسيوم، المنغنيز، الكالسيوم و الصوديوم) والمكونات البيولوجية (كوتشي، عصيات، سبيريلا، و فيبريو) فى الحمأة الخام تم إزالتها بواسطة زيادة درجة الحرارة و إجراءات غسل بالحمض يقترح جهازالموصورة "فوريه" لتحويل طيف الأشعة تحت الحمراء (FTIR) مجموعة الهيدروكسيل، الكربوكسيلات و أليفاتيك ميثيل كمجموعات وظيفية تفاعلية محتملة من الممتزات. تم اختيار الممتزات 2Z-700-90 في نهاية المطاف على أساس الصفات التي تحل محلها في العائد من 70٪، والقدرة الحرارية العالية من 50٪ و (BET) مساحة سطح 385 متر مربع / جرام. تم تحقيق كفاءة إزالة ميثيل ثلاثي بوتيل الأثير Z-700-902 في 70٪ في الظروف المثلى لدرجة الحموضة 6، سرعة التحريك من 150 دورة في الدقيقة، 60 دقيقة من وقت الاتصال، 2 جرام / لتر جرعة من الممتز والتركيز الأولي ميثيل ثلاثي بوتيل الأثير من 1 كجزء من المليون. سلوك الامتصاص من الكربون المنشط المنتج من حمأة مياه الصرف الصحي تطابق بشكل أفضل في نموذج ردود الفعل من الدرجة الثانية الزائفة. وأظهر هذا العمل الاستخدام المفيد لمواد النفايات البيولوجية مثل حمأة مياه الصرف الصحي في تكنولوجيا معالجة تلوث المياه.

CHAPTER 1

INTRODUCTION

1.1 GENERAL INTRODUCTION

The design of the novel and cost effective technologies for waste management are borne out of the rising concern and awareness of the environmental issues (Hejazi et al., 2003; Mrayyan and Battikhi, 2005). The volume of annually generated municipal and industrial sludge is massive and its disposal options are very costly from financial, social and environmental points of view (Hejazi et al., 2003; Zabaniotou and Theofilou, 2008).The estimated annual volume of dried sludge generated in Saudi Arabia is approximately 13 million tons while the reported estimate of China waste generation is approximately 80 million m^3 per day and 5.6 billion tons per year with a probable annual increase of 10% (Fang et al., 2010; Study et al., 2005). Although diverse options of sewage disposal methods and utilization are available, ranging from water body disposal, land filling, road surfacing (Jarrah and Siddiqui, 2012), incineration, land farming and application (Hejazi et al., 2003), fertilizer, crop growth enhancer and in molding the building blocks, the predominant sewage disposal method in the Kingdom of Saudi Arabia is land filling(Ouda et al., 2015). Some of the carbonaceous adsorbents have been applied in the management of air and industrial stack emission of some specific Volatle Organic Compounds (VOCs), (Chiang and You, 1987) , H_2S, (Bagreev and Bandosz, 2002) NOx, SOx, (Pietrzak and Bandosz, 2008) as well as in the treatment of the municipal and urban waste water such as phenols (Dabrowski et al., 2005;

Daifullah and Girgis, 1998) with remarkable outcome (Otero et al., 2009; Yu and Zhong, 2006). Several attempts have also been made to produce activated carbon from different organic sources.

In the same vein, Methyl tert-butyl ether (MTBE) is recognized as one of the groundwater pollutants and a potential human carcinogen by USEPA (Pankow, J. , Korte, N., 1997). It has though been tentatively listed as possible human carcinogen, its ecotoxicological health effect in lower animals such as zebra fish, clams, and other marine biota has been well established (Bonjar, 2004) and (Moreels et al., 2006). One of the sustainable, economical and much-sought after approaches for sludge disposal is the generation of activated carbon- AC- (carbonaceous adsorbent) from sludge through pyrolysis (Bagreev et al., 2001; Fang et al., 2010). It has been proven that abundant and copious amount of carbons that can be thermally or chemically converted into AC are found in the sludge of biochemical origins (Julcour Lebigue et al., 2010; Martin et al., 2002) . Chemical activation of sludge has been achieved with the use of chemical reagents like sulfuric acid, Hydrochloric acid, potassium hydroxide and zinc chloride and the resulting adsorbents have been highly remarkable in wastewater treatment (Molina-Sabio et al., 1995; Sheha et al., 2013; Wu et al., 2005). Physical activation of sludge using steam has also been experimented and its resulting activated carbons have been applied in pollutants removal and toxic emission treatment with good performance in ideal condition (S Rio et al., 2006).

1.2 BACKGROUND

1.2.1 Sewage Sludge

The main sewage sludge constituents are fats, protein, urea, silica, cellulose, nitrogen, calcium oxide, phosphoric acid, alumina, potash, magnesium oxide, heavy metals and various minerals (Izrail and Turovskiy, 2006). The two main functions determining the sewage sludge composition are the materials provenance and the adopted treatment methods (Table 1). By a way of comparison, secondary sludge is chiefly made up of microbial sources with little inorganic remnant from nitrogen, protein and phosphorous and a lower content of fats and cellulose. The biochemical conversion of plants and animal remains yield humic substances (Gascó et al., 2005). They are commonly found in the wastes of organic origin and hence their occurrence in sewage sludge. Humic substances can be classified into three on account of their solubility: fulvic acid, humic acid and humin. Fulvic acids are soluble in acid solution and are of low carbon content; it is the most highly oxidized with the lowest molecular weight (<10000). Humic acids have high molecular weight (>10000) materials, higher aromatic group proportion and are polymeric in nature and are relatively rich in carbon (Méndez and Gascó, 2005). Humin is insoluble in water owing to its possession of strong bond with the mineral fraction (Gascó et al., 2005). Gascoet. al (Méndez et al., 2005) carried out a study on four sewage sludge and discovered that the humic and fulvic acid contents of the sludge's organic components were respectively analyzed to be 4 and 20%. It was also found that these humic-fulvic abundance or ratio in the sludge is independent of the its source but can rather be strongly correlated with the sludge type and humic-fulvic acid ratio called polymerization index. Raw wastewater sludges possess high polymerization index, while anaerobically digested sludge is characterized with low ratios**.**

Table 1. Typical composition and properties of sewage sludge

Item/sludge	Untreated primary		Digested primary		Activated range
	Range	Typical	Range	Typical	
Total solids (TS) %	2.0 – 8.0	5.0	6.0 – 12	10	0.83 – 1.16
Volatile solids (% of TS)	60 – 80	65	30 – 60	40	59 – 88
Fats and grease (% of TS)					
Ether soluble	6 – 30	-	5 – 20	18	-
Ether extract	7 – 35	-	-	-	5 – 12
Protein (% of TS)	20 – 30	25	15 – 20	18	32 – 41
Nitrogen (N, % of TS)	1.5 – 4	2.5	1.6 – 6.0	3.0	2.4 – 5.0
Phosphorous (P_2O_5, %TS)	0.8 – 2.8	1.6	1.5 – 4.0	2.5	2.8 – 11.0
Potash (K_2O, % of TS)	0.1	0.4	0.0 – 3.0	1.0	0.5 – 0.7
Cellulose (% of TS)	8.0 – 15.0	10.0	8.0 – 15.0	10	-
Iron (not as sulfide)	2.0 – 4.0	2.5	3.0 – 8.0	4.0	-
Silica (SiO_2, % of TS)	15.0 – 20.0	-	10.0 – 20.0	-	-
Organic acids (mg/l)	200 – 2000	500	100 – 600	3000	1100 – 1700

Source: –Metcalf et.al (Metcalf $Eddy, Inc., Tchobanoglous, G., Burton, F. L., Stensel, 2003) from EPA (U. S. Environmental Protection Agency. 1979)

1.2.2. Activated carbon production from raw sewage sludge

The step-wise processes involved in the production of activated carbon from sewage sludge are dewatering, pyrolysis or carbonization (which can be generally termed drying) and activation of the pyrolyzed sludge. The step-wise techniques are discussed below:

1.2.2.1. Sludge dewatering

The process of removing water from a semi-liquid raw sludge sample to form a solid waste or sludge cake is called sludge dewatering. The processes that are commonly employed in dewatering include centrifuges, vacuum filters and belt presses. The most efficient dewatering treatments are centrifuges and filter presses, which may lead to total solid concentrations as high as 35% (Smith et al., 2009; Uggetti et al., 2010).

1.2.2.2 Drying of sludge

Drying of sludge entails the reduction of its moisture content through the application of thermal energy far below what is obtainable by conventional dewatering treatments. Heating methods are usually adapted to pyrolyze the sludge(Metcalf et al., 2003).

1.2.2.3 Activated Carbon (AC) Synthesis

Carbonization-activation process of sewage sludge under controlled experimental conditions yields a carbonaceous material with a high level of porosity with an extended particulate surface area(Bansal, 2005). This is the definition of activated carbon produced with physical activation method, a material that is now widely used as adsorbent in pollution treatment. Partial combustion or thermal decomposition of the sludge creates pores on the resulting activated carbon. The physical production of activated carbon involves two processes viz: carbonization of the parent material and activation of the material formed. The chemical methods of producing activated

carbon involves treatment of the parent material with acid, base or salt followed by contact with controlled atmosphere to aid in the activation process. It requires less amount of heat compared to the physical process of producing activated carbon.

1.2.2.4. Carbonization / Pyrolysis

This is the process of subjecting the carbonaceous materials into higher temperature ranges of about 500-800 ^{0}C under an inert environmental condition using N_2 gas. The characteristics (i.e. BET surface area and pore volume) of the produced char depend mainly on temperature and dwell time of the pyrolysis process. The material's thermal decomposition realized from this process serves to drive out other elemental constituents aside carbon as volatiles (Bansal, 2005). It regroups and reshapes the elementary carbon freed atoms as irregularly arranged graphitic crystallites (Bagreev et al., 2001; Che et al., 1999). The existing interstices between the crystallites yield rudimentary pores and ergo many of which may be choked by residues or scattered carbon (Bansal, 2005). Activated carbon is widely known for its monumental adsorptive capacity; a gram of activated carbon contains an area of around 500m^2 while a pound of activated carbon contains an area equal to six football pitches.

1.2.3. AC Activation methods

There are three main distinct methods of activating carbons; these are physical, chemical and biological activations.

1.2.3.1 Physical activation

Physical activation is the selective oxidation of atoms from the carbon structure through controlled gasification. It proceeds by the progressive burning-off of the carbon fraction. The thermal oxidation is achieved through the exposure of carbon interstices to an oxidizing gas at 700–1100

^{0}C. This further serves to eliminate the tarry substances blocking the pores. However, the inorganic content of sludge is much. Consequently, activated carbon that has been produced through physical activation, stereotypically exhibits relatively low surface area (Smith et al., 2009). The characteristics (i.e. yield, BET surface area and pore volume) of the produced activated carbon depend mainly on the gas that is used for temperature, dwell time and nature of the activation agent. Different activating gases such as air (A. Ros et al., 2006) , CO_2 (Jindarom et al., 2007; a. Ros et al., 2006) and steam (Fitzmorris et al., 2006; S Rio et al., 2006) were studied. Data, regarding BET surface area, reveal that steam is the best physical activation gas. The highest BET surface area achieved was 226 m^2/g (S Rio et al., 2006). Using the response surface methodology, BET surface area was maximized at an activation temperature of 763 ^{0}C and a dwell time of 39 min. However, the conditions were 790 ^{0}C and 70 min to maximize the pore volume (S Rio et al., 2006). In order to enhance the BET surface area of the physically activated sludge, washing with acid was investigated. Washing the char with HCl before activation resulted in an increase in BET surface area from 7 to 269 m^2/g (A. Ros et al., 2006).

1.2.3.2 Biological Activation

Biological Activated Carbon's (BAC) adsorption is premised on biodegradation and subsequent adsorption processes of the target organic pollutants. BAC employs the use of granular activated carbon (GAC) as ultimate adsorbents of organics and as a support or biofilm for biodegrading microbes (Ahmed et al., 2007; Zhang et al., 1991). Powdered Activated Carbon (PAC) is also employed in the pollution treatment technologies when added to the activated sludge (Aktas and Cecen., 2007; Sublette and Sylvester, 1982). The mechanisms of biological activation of the carbon bed were based on an unproven unified old hypothesis of bioregenerative desorption of BAC through exoenymatic reactions. The mechanisms stated that activated carbon be partially bio-regenerated through the actions of some microorganisms; the less biodegrable organics can firstly be adsorbed onto the carbon and subsequently degraded through

exoenzymatic reaction and that the enrichment of the organics via adsorption increases the biological activities of the degrading microbes. The hypothesis was subjected to tests and found unsubstantiated especially when (Zhang et al., 1991) considered some of the properties of enzymes involved in the biodegradation pathway of aromatic hydrocarbons and phenols. Investigative BAC column tests were performed to assess the changes in its carbon adsorptive ability during the operation and Warburg respirometer was employed to evaluate the properties of the biological activities. It was concluded that combined effects of biodegradation and carbon adsorption were responsible for the mechanism of BAC process. Specially designed Biological Aerated Filter can be employed in an advanced water treatment technology.

1.2.3.3 Chemical Activation

This is the process of adding chemical activation reagent to the carbonaceous material and then heating the mixture under an inert condition to a temperature point sufficient enough to cause a systemic reaction. The processes (pyrolysis and activation) progress simultaneously in chemical activation methods in contrary to physical activation that has intermittent order of processes. The characteristics (i.e. yield, BET surface area and pore volume) of the produced activated carbon depend mainly on four factors: dwell time, nature of the reagent, temperature and reagent-sludge mixing ratio (Smith et al., 2009). Different chemical reagents were used such as: KOH, NaOH, $ZnCl_2$, H_2SO4 and H_3PO_4. Table 2 shows that the most effective reagents are KOH, NaOH and $ZnCl_2$. However, these studies were done at different pyrolytic conditions, pre-treatment and post-treatment. To the best of my knowledge, there is no systematic study that compares the efficiency of activating agents. The optimum temperature is related to time of activation. High temperature requires less time of activation. There is no published work on optimizing yield and characteristics (i.e. BET surface area, pore volume and pore size distribution) of the produced activated carbon.

Table 2: Properties of activated carbon produced by chemical activation of sludge

Activation agent	Agent/sludge ratio	Temperature (°C)	Dwell time (min)	BET surface area (m^2/g)
KOH	1:1	700	60	1882
KOH	Soaked in 3M KOH	600	60	382
KOH	3:1	700	60	1686
KOH	1:1	700	60	1301
NaOH	3:1	700	60	1224
$ZnCl_2$	10 g in 25 ml 5M $ZnCl_2$	500	2	647
$ZnCl_2$	3.5:1	800	120	1092
$ZnCl_2$	1:1	650	5	472
$H2SO_4$	100 g in 250 ml 3M H_2SO4	650	60	408
$H3PO_4$	100 g in 250 ml 3M H_3PO4	650	60	289

Source : (Julcour Lebigue et al., 2010)

1.3. METHYL TERT-BUTYL ETHER (MTBE)

1.3.1 General Characteristics of MTBE

MTBE is one of the popular oxygenates used as fuel additive and solvent in a lead-free gasoline to improve the octane rating, enhance complete fuel combustion that will ultimately prevent emissions of toxic gases associated with premature oil combustion. It is an ether derivative synthesized from methanol and isobutylene. It is volatile, lipophilic, colorless, flammable, and a water soluble compound that persists in soil, water and air when released during petroleum fuel cycle (Lien and Zhang, 2007; Rengaraj, 2002). Gasoline to which MTBE is added is usually referred to as oxygenated gasoline. The low cost and readily simple production makes MTBE suitable candidate among other oxygenates. However, the persistent nature of MTBE makes it a greater and a counterproductive toxic emission inhibitor as it in itself contaminates ground water when infiltrates the aquifer, resists biodegradation and remains for longer periods at high concentration(Cassada et al., 2000; Zwank et al., 2002). Incidents of both surface and groundwater contamination by MTBE, BTEX and benzene have been widely reported in the US and other parts of the world.(An et al., 2002; Delzer et al., 1997; Reuter et al., 1998).

1.3.2 Levels of MTBE in the Environment

MTBE infiltrates the soil, percolates the adjourning unconfined aquifer and reaches the water table that holds ground water. It is highly soluble in water and slowly degrades into harmful metabolites such as Tert-butyl alcohol (TBA), Formaldehyde, Tert-butoxy methanol, 2-methyl-2-hydroxy-1-propanol, 2-hydroxysisobutyric acid, Acetone and Acetaldehyde. However, in surface water, MTBE easily gets vaporized and as a result been detected in traces than groundwater. The combined effects of physical and chemical properties make it a likely contaminant of public

drinking water system(Cassada et al., 2000)(Hong et al., 1997). Some groundwater samples analyzed for MTBE in different locations and their mean concentration ranges are as shown in Table 3.

Table 3. Mean concentration range of MTBE in groundwater samples

Groundwater (2743 samples)	Mean concentration range of MTBE
94.7%	< 0.2 μg/l
4.9%	0.2 – 20 μg/l
0.4%	> 20 μg/l

Source : (Zogorski, 2005)

1.3.3 Health Effects of MTBE

MTBE, when inhaled via respiration, is transformed into some metabolites such as butyl-alcohol, methyl-alcohol, formaldehyde, formic acid, and carbon dioxide which leave the body via exhalation or ultrafiltration processes of the kidney usually in 1 or 2 days (ATSDR, 1996). Acetone, tert-butyl-alcohol (TBA), methyl-alcohol, formaldehyde and carbon(IV)oxide are the metabolites of MTBE if the exposure is through other routes like oral, dermal, et. c. (Lenczewski et al., 2007). Animal studies have shown that MTBE is rapidly absorbed following oral or inhalation exposure, distributed in the blood to all parts of the body, including the brain and highest tissue levels were reported to occur in liver and kidneys. Acutely toxic oral doses can result in nervous system effects as well as muscular weakness and inflammation of the stomach and small intestines, as reported from experimental study of rodents with oral (lethal dose) LD50 values of 1.6-3.9 g/kg. Inhalation exposure resulted in inflammation of nasal mucosa and trachea. Similarly,

blood chemistry changes and kidney abnormalities were observed in laboratory rodents exposed to high doses or concentrations of MTBE. However, limited information indicate that ambient levels of MTBE do not pose a health risk to healthy individuals, although susceptible population living under unique climatic condition such as sub-arctic may be adversely affected (ATSDR, 1996).The potential carcinogenicity of MTBE in humans is unconfirmed because of limited information. However, it is classified by the US Environmental Protection Agency as a possible human carcinogen based on limited animal results of renal tubular cell tumors (adenomas and carcinomas) upon exposure to MTBE while varying the concentrations and exposure duration (USEPA, 2007).

Developmental, reproductive and neurotoxicity were observed in laboratory rodents exposed to high concentrations of MTBE, with limited information available on its potential effects on humans. Increase in maternal mortality, as well as significant reduction in mean pup weight throughout lactation was observed in laboratory two generation study conducted on the same stain of rats (Dongmei et al., 2009). Neurotoxicity effects reported from laboratory study of mice included blepharospasm, hypoactivity, ataxia, lack of startle reflex, stereotypy, and prostration (Burbano et al., 2008). MTBE is expected to show low acute toxicity to aquatic organism, although limited information is available and the lethal concentrations are generally greater than 100 mg/L. Same information constraints exist with toxicity to terrestrial organism, although the oral LD50 values of 1.6-3.9 g/kg for rats suggests that only when present at very high concentrations would the chemical be acutely toxic to terrestrial organisms. Also, as per the definition provided by the Agency for Toxic substances and Disease Registry, (ATSDR, 1996), MTBE is a volatile organic compound and as such can contribute to the formation of photochemical smog in the presence of other VOCs. Owing to the aforementioned lethal effects of MTBE on the main components of the

environments, several environmental protection agencies in the United states and across the world have put regulations on MTBE exposure in the environment (Table 4).

Table 4. Regulation levels of MTBE in some environmental protection agencies in the US and KSA

Agency	**Type of Regulation**	**Regulation Levels**	**Effective date and reference**
USEPA	Drinking Water Advisory	20-40 ppb	12/1997 (USEPA, 2007)
ATSDR	Acute Inhalation Minimal Risk Level Chronic Inhalation Minimal Risk Level Acute Oral Minimal Risk Level Intermediate Oral Minimal Risk Level	2.0 ppm 0.7 ppm 0.4 mg/kg/day 0.3 mg/kg/day –	08/1996 (ATSDR, 1996)
California	Secondary MCL EPA complete Ban	5.0ppb	01/07/1999 12/31/2003 (USEPA, 2007)
Iowa, South Dakota	EPA Partial Ban	No more than trace amounts (0.5% by vol.) MTBE.	5/11/2000 2/28/2001 (USEPA, 2007)
PME (KSA)	Discharge limits for effluents prior to discharge into water bodies (Red sea, Gulf and surface water).	0.01 ppm	24/03/2012 (Presidency of Meteorology and Environment, 2011)

1.3.4 Environmental Degradation

The reduction in concentration of MTBE in the environment can occur naturally or be enhanced by human interference. When in the atmosphere, MTBE may remain in its gaseous state until washed down by precipitation. The average lifetime in the atmosphereis 4 days, before degradation by reaction with hydroxyl radicals (OH·) or photolysis by penetration of ultraviolet (UV) light from the sun. Degradation by hydroxyl radicals results in the formation of tert-butyl-formate (TBF), methyl-acetate, acetone, TBA and formaldehyde; while degradation by photolysis results in carbon dioxide and water formation (Kinner et al., 2001)

1.4 PROBLEM STATEMENT

The environmental and legislative constraints imposed on land filling, increasing rate of sludge production coupled with the availing restricted disposal options, depletion of land resource and poor effort in the reclamation agenda among other reasons call for more efficient, cost effective and environmentally friendly approaches to managing waste. In addition, the complexity involved in the preparation of carbonaceous adsorbents and high cost of production of these products are among some of the drawbacks challenging the use of Commercial Activated Carbons as absorbents of water pollutants. More so, one of the sources of groundwater contamination has been linked to the leakage of MTBE from the oil pipeline, gasoline stations, leaking underground storage tanks (Protection., 2001), et. c.

1.5 SIGNIFICANCE OF STUDY

Developing a cost effective, environmental friendly and a sustainable use of SDAC in water treatment will make this study highly significant. In addition, MTBE is a peculiar pollutant of the oil-producing countries and leaving it unaddressed may pose potential danger to human and animal's health. In the same vein, available adsorbents (Commercial Activated Carbon) are costly and as a result, a novel way of converting cheaply available waste into adsorbent that can serve the same purpose of the CAC will be a welcome idea.The use of MTBE among other oxygenates in the petroleum fuel cycle has been banned by USEPA and tagged as a possible human carcinogen for its obvious negative health impacts on lower animals, though the ban campaign in Saudi Arabia is still under debate.

1.6 RESEARCH OBJECTIVES

The main objective of this study is to evaluate the removal efficiency of sewage sludge-based Activated Carbon (SDAC) for MTBE – contaminated water. The specific objectives are;

- To synthesize and characterize the activated carbon derived from the sewage sludge.
- To demonstrate the removal of MTBE from contaminated water using the optimized SDAC.
- To study the effect of solution conditions such as pH, SDAC dosage, contact time, and MTBE concentration on the adsorption efficiency.
- To evaluate the adsorption isotherms and kinetics under the optimum treatment conditions.

CHAPTER 2

LITERATURE REVIEW

A broad review of published works on sewage sludge-based adsorbents (SBAs) has been painstakingly written and published by a team of scientists led by Smith (Smith et al., 2009). The review covered the production processes, properties and the applications of SBAs in water treatment. The paper is a repository of essential data and cogent information needed for further research on the topic. Evaluation and assessment of a viable and economic means of producing SBAs on a large scale within the context of sustainable measures are recommended.

2.1 SLUDGE-DERIVED ACTIVATED CARBON

Sewage sludge is cheaply generated in large quantities especially during the biological wastewater treatment processes. The most challenging task is in prioritizing the best among all the available sewage disposal options. Most common of the disposal options are landfill (Ouda et al., 2015), land application, agricultural use (Hossain et al., 2011; Méndez et al., 2012), incineration and recycling (adsorbent production) (Inguanzo et al., 2002; Julcour Lebigue et al., 2010; Wen et al., 2011). In view of increasing stricter environmental law and constraints, increasing sludge production and limited disposal option, production of carbonaceous adsorbents from sludge in pollution management and sciences has received great attention (Bansal, 2005; Dabrowski et al., 2005; Fang et al., 2010; Jaramillo et al., 2010; Martin et al., 2002; Removals, 2007)(Pietrzak and Bandosz, 2008; S Rio et al., 2006; Sheha et al., 2013).

There are recent copious studies on assessing the adsorptive capacity of sewage sludge-derived activated carbon on many organic pollutants. Some of these studies are briefly discussed below:

In a recent work of (Gu et al., 2013), sewage sludge derived porous activated carbon was applied for adsorption and degradation of naphthalene dye intermediate(1-diazo-2-naphthol-4-sulfonic acid (1,2,4-Acid) using peroxide as oxidant. After a 2-hour treatment, a successful removal of 94% of initial concentration of 150mgL-1 1, 2, 4-Acid was recorded. SDAC has also been used to remove phenol and carbontetrachloride (Chen et al., 2002). The results indicated remarkable micropore and mesopore surface areas and notable adsorption capacities for both pollutants. Table *5* shows summary of the uses of sludge materials as adsorbents of various pollutants.

In another scholarly research by (Zhang et al., 2005), organic sewage sludge-derived activated carbon was also applied to treat mercury-contaminated water. Here, three different chemical activation reagents (H_2SO_4, H_3PO_4 and $ZnCl_2$) were used to produce various types of activated carbons and these were in turn applied in the removal of Hg (II) from aqueous solution. Chemical activation dramatically improved the quality of the produced activated carbons and the highest Hg (II) adsorption capability recorded in the $ZnCl_2$ activated carbon.

Sewage sludge-derived activated carbon has also been applied in a combined activated sludge-powdered activated carbon treatment (Martin et al., 2004; Sublette et al., 1982), in the treatment of Pb(II) (Goel et al., 2005), organic materials in water (Yu and Zhong, 2006), hybrid water treatment (Julcour Lebigue et al., 2010), thiophenic compound from oil (Yu et al., 2013), dye removal (Jindarom et al., 2007)et.c. From the literature search so far, no single work on investigative study of the sewage sludge-derived activated carbon capability in the removal of MTBE in aqueous solution was found.

2.2. MTBE REMOVAL TECHNOLOGIES

2.2.1. Chemical Oxidation

Here, oxidizing agents such as chlorine, hydrogen peroxide (H_2O_2), Fenton reagent (H_2O_2 and Fe (II) and ozone O_3 are used to degrade contaminants. Fenton reagent is considered the most effective of chemical oxidation techniques as it degrades 99% of initial MTBE concentration of 15mM at 120min and a pH of 2.8 to yield low concentrations of TBA and acetone (Xu et al., 2004). Fast degradation of MTBE was reported in a study with bifunctional aluminum obtained by sulphating aluminum with sulphuric acid. TBF, TBA, methyl acetate and acetone were the by-products from the treatment process(Ahmed et al., 2007). A detailed research work on the effect of oxidant-to-substrate ratios on the degradation of MTBE with Fenton reagent was also reported by Burbano and his team (Burbano et al., 2008)

2.2.2. Advanced Oxidation Processes (AOPs)

These remediation techniques exploit the principle that MTBE can be physically or chemically converted into CO_2 and water. In these technologies, powerful oxidants such as free hydroxyl radicals (OH^-), exited ozone are generated to knock off or break down the complex structure of contaminants in aqueous solution to produce less harmful by-products. A combination of different techniques such as ultraviolet radiation (UV), ozone (O_3), hydrogen peroxide, photo-Fenton (Fe^{2+}) and titanium dioxide (TiO_2) are the major AOP techniques used for different drinking water treatments(Burbano et al., 2008; Tawabini, 2014; Wu and Lin, 2007). The main challenge of adopting this remediation technique in treating MTBE is in the production of less degradable by-products such as acetone, methanol, formaldehyde, TBF and TBA during the process (Ã and Young, 2000).

2.2.3. Biodegradation

This is a microbial mediated process for the treatment of MTBE contaminated water resources. Biotransformation processes of MTBE are slow and isolation of degrading organisms is difficult, creating a problem with this remediation method. Several studieshave reported high stability of MTBE under anaerobic and aerobic conditions (Deeb et al., 2000; Stefan et al., 2000). There is little known about the biological fate of gasoline oxygenates, despite the established biodegradation research of many gasoline components. In a review of studies on biodegradation of MTBE, higher decomposition rates were reported under aerobic conditions (Deeb et al., 2000; Kane et al., 2001). MTBE biodegradation of 89% was reported in an in-situ case study in which oxygen curtain technology was employed (Levchuk et al., 2014) The presence of ethylbenzene and xylene was reported to severely inhibit MTBE biodegradation. Similar result was obtained in another study where toluene and xylene were reported to significantly inhibit MTBE biodegradation, while less inhibitory behavior was reported with TBA and ethylbenzene (Wang and Deshusses, 2007; Yang et al., 2010).

2.2.4. Electrochemical Oxidation

The available reports on electrochemical oxidation of MTBE are few. Iridium dioxide coated electrodes have been successfully used to degrade MTBE (Wu and Lin, 2007)(Wu, 2011). It was observed that the most efficient MTBE removal was achieved in acidic conditions. At operating potential of 3.0V with sulfuric acid as electrolyte, 92% of MTBE with initial concentration of 20 mg L^{-1} was removed after 3hours with the determination of TBA, acetone and CO_2 as by products (Wu and Lin, 2007). Nickel electrode was also used to achieve 73% removal efficiency of initial MTBE concentration of 20 mg L^{-1} after 3hours (Wu, 2011). Optimum conditions for alkaline at

operating potential of 0.35 V and 1 M KOH solution was also reported. Formation of $NiOOH/Ni(OH)_2$ layer on the surface of anode was observed and there is tendency for this layer acting as mediator on decomposition of MTBE.

2.2.5. Air Stripping

In the treatment of groundwater contaminated with volatile organic compound, air stripping is a well-established process, with several successful applications in municipal wastewater treatment(Smith et al., 2009; Stefan et al., 2000). When compared to benzene, 2 to 5 times more air is required for treatment of same amount of MTBE contaminated water with below 5 µg/L concentration. This is an ex-situ (pump and treat) remediation technique for groundwater sources contaminated with MTBE. Given the solubility and hydrophilic properties of MTBE pump and treat techniques are considered effective in its remediation. Air stripping involves the use of inert gas for MTBE removal from contaminated water sources. This technique is not economically feasible because MTBE has affinity for aqueous phase than gaseous phase.

Another important consideration with air stripping is that it transfers MTBE from one phase to another; therefore further treatment of the gaseous phase is required. (Stefan et al., 2000) reported that heating the contaminated water as well as reduction in overall pressure of air stripping system improves the effectiveness of MTBE removal by this technique, due to increase in the Henry's constant. Air stripping has been reported by some researchers as non-economical for treatment of MTBE contaminated water sources (Bousba and Hassen, 2014). Removal efficiencies of more than 90% were reported in a study on the application of air stripping for treatment of MTBE contaminated drinking water, with air stripping mostly combined with other treatment methods such as adsorption with activated carbon in most studies (Dabrowski et al., 2005).

2.2.6. Adsorption

Adsorption is one of the promising techniques for the removal of synthetic organic compounds from many contaminated environmental media with broad applications (Weber et al., 1991). Having tested successfully for the removal of MTBE from contaminated water, Granular Activated Carbon (GAC) is popularly employed as adsorbents of many contaminants (Shih et al., 2003);(Rengaraj, 2002) and (Goel et al., 2005) However, a challenge with this technique is the poor removal efficiency that may be observed especially when other synthetic organic compounds co-exist with MTBE, rendering the carbon adsorption process less cost-effective for MTBE removal (Pietrzak and Bandosz, 2008). Another constraint is that the presence of natural organic matter may slow down the adsorption kinetics and reduce the adsorption capacity while applying activated carbon in natural water. Various examples of adsorption technologies are fly ash adsorption, Ion Exchange Resin, Zeolite, granular activated carbon, and sewage sludge derived activated carbon. Different pollutant removal technologies and their respective capacities in adsorbing MTBE are listed in Table 5 . The tested adsorbents for treating MTBE-contamiated water are also listed in Table 6

Table 5. Some existing contaminant removal technologies in the world

Technology	Specific (vendor/producto r material)	Initial MTBE concentration (mg/l)	Removal capacity (mg/g) or efficiency (%)	Reaction by-product[1]	Experimental conditions	Reference
AOPs	Fenton's reagent	88.2	99%	a, b, e, f	Batch test	(Xu et al., 2004)
	O_3/H_2O_2	0.012	>99%	a, b	Batch test	(Acero et al., 2001)
	UV/ H_2O_2	81.1	>99%	a-f	Batch test	(Stefan et al., 2000) (Tawabini and Zubair, 2011)
	Bifunctional Al^0	14.2	90-99%	a, b, e, f	Batch test	(Lien and Wilkin, 2002)
Nafion	Nafion SAC-13	50	70%, sorption	b, e, g	Batch test	(Lien and Zhang, 2007)
Electrochemical Oxidation	Iridium- dioxide coated electrodes	20	92%	b, e, h	Column test	(Wu and Lin, 2007)(Wu, 2011)
	Nickel Electrodes	20	73%	b, e, h	Column test	(Wu, 2011)
GAC adsorption	Calgon/PCB	0.02	0.14-0.22mg/g	None	Column test	(Shih et al., 2003)
	US filter/CC602	0.02	0.11-0.19mg/g		Column test	(Shih et al., 2003)
	Calgon/F400	0.02-0.05	0.46-0.69mg/g		Batch test	(Yu et al., 2005)
	Calgon/F600	0.02-0.05	0.56-1.43mg/g		Batch test	(Yu et al., 2005)
SDAC	Sewage sludge	?	?	?	Batch test	This work

[1]Byproducts: (a)*tert*-butyl formate (TBF); (b)*tert*-butyl alcohol (TBA); (c) 2-methoxy-2-methyl propionaldehyde (MMP); (d) formaldehyde; (e) acetone; (f) methyl acetate; (g) isobutene. (h) CO

Table 6. Available adsorbents for treating MTBE-contaminated water

References	Description	Main results
(Adebayo et al., 2016)	Investigated the removal of MTBE from water using raw and modified fly ash (FA) waste materials	silver oxide (Ag2O) impregnated FA achieved ~24%
(Ji et al., 2009)	Tested the removal of MTBE using porous polymeric adsorbents	Adsorption efficiency of the postcrosslinked polymer towards MTBE is attributed to its high surface area, large micropore volume and moderate hydrophility
(Rossner and Knappe, 2008)	Assessing the effectiveness of silicalite zeolite, a carbonaceous resin, and a coconut-shell-based granular activated carbon (GAC) for the removal of MTBE from water	Both the silicalite zeolite and the carbonaceous resin exhibited larger MTBE adsorption uptakes than the tested GAC.
This work	Evaluating the removal efficiency of Sewage Sludge-Derived Activated Carbon in MTBE – contaminated water	?

2.3 RESEARCH GAP

In view of the reiterated limitations of the existing commercial adsorbents, sourcing for reduced cost processes that will yield adsorbents of high specific surface area with ease of synthesis will be an indispensable panacea. This will assist in cleaning up our environment, keeping it free of toxic and unpalatable emissions, and at the same time encouraging resourceful use of waste. Although, sewage sludge-derived carbons have been used as adsorbents for many organic and inorganic pollutants as shown in Table 7, no work was found on its use for MTBE removal from contaminated water.

Table 7 Various pollutants removed by SDAC

References	Application	Result
(Chen et al., 2002)	*__SDAC__ has also been used to remove **phenol and carbontetrachloride** (CCl_4)	remarkable micropore and mesopore surface areas and notable adsorption capacities of 2.69mg/g for phenol and 4.5mg/g for CCl_4.
(Lien and Zhang, 2007)	Chemically activated **SDAC** used in the treatment of **mercury-contaminated** water	Highest Hg (II) adsorption capacity of 0.56 – 1.46mg/g recorded for the $ZnCl_2$ activated carbon
(Lu et al., 2013)	**SDAC** was used for the removal of **DBT** from n-octane. Time (30mins-2hrs), Carbonization temperature (400-800°C), Different activating agents	Adsorption increases with increase in C=O functional groups. 70.6% DBT was removed using KOH activating agent carbonized at 600°C for 1hr.
(Gu et al., 2013)	Adsorption (SDAC) and degradation of **naphthalene dye intermediate (1-diazo-2-naphthol-4-sulfonic acid (1,2,4-Acid)** using peroxide as oxidant and subsequent adsorption	Successful removal of 94% of initial concentration of 150mgL^{-1} 1, 2, 4-Acid was recorded.

*SDAC : Sludge-Derived Activated Carbon

CHAPTER 3

RESEARCH METHODOLOGY

3.1 CHEMICALS AND EQUIPMENT USED

MTBE, a product of Sigma-Aldrich, Saudi Arabia, with 99.999% purity (HPLC grade) was used for the study. Ultrapure Deionized water generated from a Mili-Q purification system was used to prepare 100ppm of MTBE stock solutions, a consignment where a measured solution was taken to prepare a spiked sample prior to treatment. Two activation reagents used for the study-$ZnCl_2$ pellet (99.99% purity) and KOH pellet AR (99.9% pure)- were of the analytical grades purchased fresh from Panreac Quimica, Alpha Chemical, EU. Sulphuric acid solution (H_2SO_4) (Chem-Lab NV), HCl acid solution, NaOH (Chem-Lab NV) and nitrogen gas (99.99% purity) were respectively used to adjust the pH and to create an inert environmental condition for carbonization.

The physical properties of the sludge (dry and wet samples) such as the particle size, moisture content, ash contents, total heavy metals, pH, Alkalinity, total organic carbon and oil and grease were determined using the lists of equipment and standard methods shown in Table 8.

Table 8. Physical properties of sludge and the equipment used to analyze them

Parameters	Method	Equipment and reagents	Remarks
Particle Size	ASTM D-2862-97	Sieve USA Standard Test Sieve (500µm and 250µm mesh size)	Standard Test Method for particle size distribution. (Sludge sample & AC)
Moisture Content	Gravimetric/oven drying method ASTM D 2867-09	Oven (Heratherm 3.75 cu. ft. (105 L) General Protocol), the crucible with covers and desiccators.	Moisture content determination for sludge sample.
Ash Content, Total Fixed Cabon	ASTM D 8266-94	Oven, Muffle furnace (ST-1200RG-4, SuTong China) and Desiccators	This stands the latest method of ash content determination.
Heavy metals	USEPA 820 Microwave-assisted digestion and Inductively coupled plasma mass spectrometry analysis	Conc. HNO_3 (Chem-Lab NV), and Microwave irradiated closed vessel system were used for digestion and Agilent ICP-MS 7700 was used for heavy metal analysis.	ICP-OES can also be used for the analysis.
Total Organic Carbon (TOC)	Indirect method of TOC analysis	Conc. HCl, heat plate were employed for digestion and TOC-SSM Schimatzu Analyzer for TOC analysis	
Oil and Grease	Microwave-assisted digestion	Microwave Digestor	

3.2 SEWAGE SLUDGE-DERIVED ACTIVATED CARBON PREPARATION

The sewage sludge sample used in this study was obtained from Dhahran Wastewater Treatment Plant (WWTP), the Eastern Province of the Kingdom of Saudi Arabia. The fresh sludge type used was the one dewatered using belt filtration technique to avoid any anaerobic digestion pretreatment and thus contained chunks of organic matter.

3.2.1 Pre-Activation sample handlings; Drying, Crushing and Sieving

The integrity of the sludge sample was preserved by collecting it in a polyethylene container prior to the lab analysis. Certain portions of the sludge were randomly sampled and mapped out of the consignment to be analysed for as-received proximate and component analyses. The remaining sample sludge was then oven-dried at 110^{o}C for 48 hours, crushed with the aid of pestle and mortal and afterward sieved with a-500μm sieve to have dried sludge of uniform particle size . The handling techniques were expected to preserve the sludge by driving out the residual moisture, and as a result prevent further biodegradation. The stepwise procedural operations involved in the production and characterization of the asorbent are as shown in Figure 1.

3.2.2 Activation stage; Chemical Activation and Drying of the Activated Sludge

Chemical activation of the sludge sample was accomplished by employing two different activating reagents; KOH, $ZnCl_2$ under different activation conditions as shown in Table 9. The activation experiment was designed using the arbitrary design of experiments (DOE) technique.

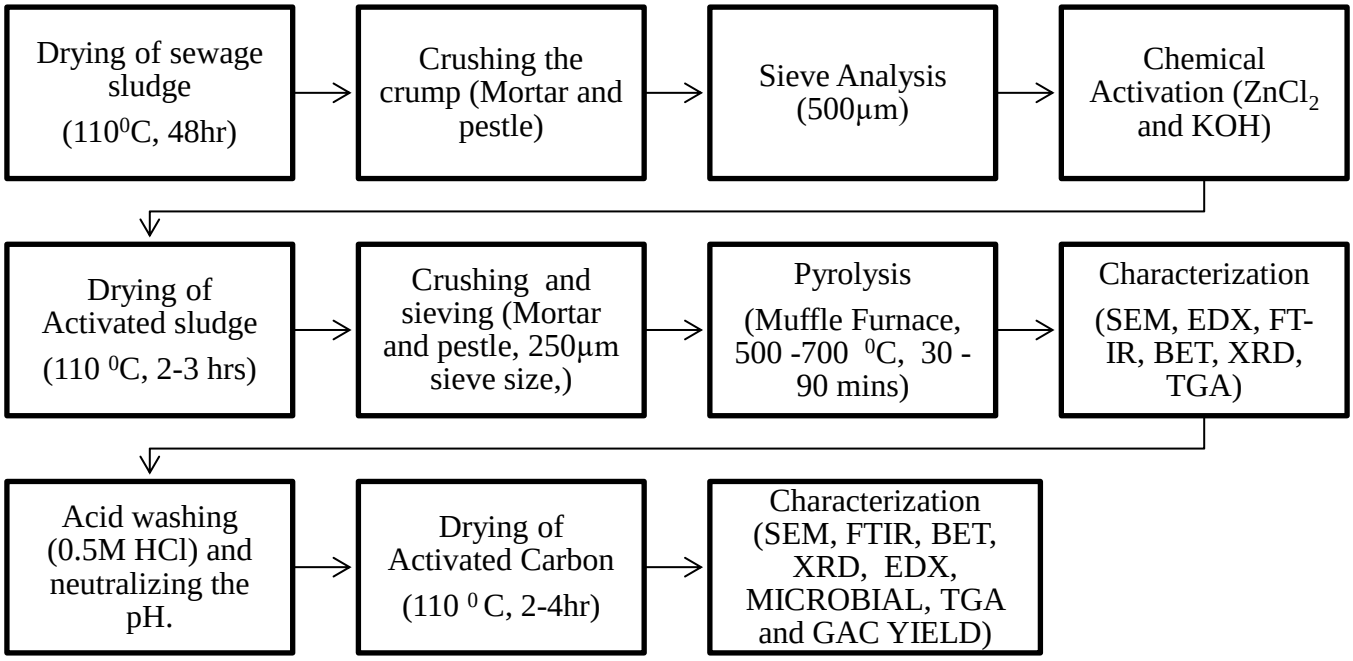

Figure 1 Procedure for Sludge-derived Activated Carbon synthesis and Characterization.

Table 9 Design of Experiment for both $ZnCl_2$-AC and KOH-AC

Appellation	Activation reagent	Reagent/Solid mixing ratio	Temperature (^{0}C)	Dwell time (min)
2Z-500-30	$ZnCl_2$	2:1	500	30
2Z-700-90	$ZnCl_2$	2:1	700	90
3K-700-30	KOH	3:1	700	30
2K-500-90	KOH	2:1	500	90

The furnace' heating rate was fixed at 10 ^{0}C min^{-1}). AC = Activated carbon.

The variable conditions of the experiment were temperature, time, and reagent/sludge ratio for each of the two activation reagents. Going by the experimental layout for the activation process and pyrolysis, a total number of four sludge samples (dried and sieved to the particle size cited in the literature) of equal weight were achieved. These samples were respectively given appellations (3K-700-30, 2Z-700-90 2K-500-90, and 2Z-500-30) based on the nature of the activation reagent, reagent to solid ratio, pyrolytic temperature and dwell times. The whole set-up was put on the Thermo Scientific dual-task heaters (@ 80 ^{0}C) and left overnight for drying.

3.2.3 Pyrolysis

The selected sludge sample was carbonized at a temperature range of 500 ^{o}C-700 ^{o}C, with the recommended dwell time-range of 30-90 minutes and at a constant heating rate of 10 ^{o}C/min, under nitrogen gas stream (flow rate of 50mLmin^{-1}) in a tubular muffle furnace (ST-1200RG-4, SuTong China) (*Figure 2*) to produce the carbon char. The produced activated carbons were then weighed on a weighing scale (Wensar HPB 1000H, 1000 gm Accuracy 0.001mg Weighing Scale) and documented accordingly.

3.2.4 Acid Washing

The carbonized powders, according to Zou and his team (Zou et al., 2013), were thoroughly acid washed with liquid/solid mass ratio of 20:1 at 80 ^{0}C using 0.5M HCl and stirred for 6-7 hours . The acid washing exercise was immediately followed by repeated water washing step using deionized water at time interval of 10 mins until the pH of the washing water reached 6-7. The supernatant-washing water- was separated from activated carbon using a centrifuge set at 3500rpm for 15min and then dried in an oven set at 100 ^{0}C for 12h. The GAC yield was later computed using the formula:

$$Y = \frac{\text{the weight of the sludge after washing}}{\text{the weight of the sludge recovered after pyrolysis}} \times 100\%$$

Figure 2. Tubular muffle furnace used for pyrolysis

3.3 COMMERCIAL ACTIVATED CARBON

The brand name of the Commercial Activated Carbon employed in this work for the comparative study is GC- IPH from the General Carbon Corporation, NJ. It is a coal based adsorbent purposely loaded for desulphurizing gases and removing acidic contaminants. Coconut shell base Activated Carbons are also available in stock. The properties of the two main constituents of GC – IPH (Carbon substrate and Impregnated carbon) are as shown in table 10:

Table 10 Basic properties of the Commercial Activated Carbon

Carbon Substrate		**Impregnated Carbon**	
Particle type	Pelletized	Bulk Density (g/cc)	0.55 (min.)
Typical Particle size Diameter (mm) Length (mm)	 4 6	Head loss @ 50 fpm face velocity through a dense packed bed, inches w.c./ft. bed depth	1.9 (max.)
Mean Particle Diameter (mm)	4.7 (min.)	Moisture	15 (max.)
CCl_4 Activity (%)	60 (min.)	Hydrogen sulfide breakthrough capacity, gH_2S/cc carbon	0.14 (min.)
Iodine Number (mg/g)	1000 (min.)		
Surface Area (m^2/g)	1000 (min.)		
Hardness (%)	95 (min.)		

The pelletized Commercial Activated Carbon (GC – IPH) was turned into powder and appropriately sieved using the sieve of equal mesh dimensions (250µm); the one employed to sieve dried SDAC. This is necessary to avoid having adsorbents of different particle sizes.

3.4 CHARACTERIZATION OF SEWAGE SLUDGE-DERIVED ACTIVATED CARBON

For a proper appraisal of the physicochemical quality of the produced physical properties of the raw sludges and the SDAC-surface morphology, their participating functional groups, thermal stabilities, and surface area- series of instrumental studies were carried out to ascertain these.

3.4.1 Proximate Analysis of the raw sludge

Proximate analysis of the raw sludge samples were analyzed in duplicates for the parameters summarized in

Table *11*. The extent of the heavy metals in the sludge is as shown in Table *12*. Sludge samples were pre-digested by mixing a concentrated HNO_3 and fresh sludge sample in a Liquid to Solid ratio of 20:1. The set up was then put inside a Microwave Digestion System's rotor (YMW-80, Changsha Yonglekang Equipment Co., Ltd) and subsequently programed for total digestion.

Table 11. Proximate Analysis of the raw sludge

	Proximate Analysis	
Parameters	**Fresh Sample**	**Dry Sample**
Moisture content (%)	84.65	15.58
Total solids (%)	15.35	84.42
Volatile solids (%)	68	67
Ash content (%)	31	30
Total Fixed (%)	32	32
Alkalinity (mg/kg)	1158	1113
TOC (mg/kg)	4523	27325
Oil and Grease (%)	609	429
pH	7.8	7.3

Table 12 Concentration of heavy metals in the raw sludge.

Elements(ppm)	Pb	Tl	Ba	Cd	Mo	Se	As	Zn	Cu	Ni
Dry Sludge	0.047	0.001	0.346	0.001	0.014	0.023	0.004	0.845	0.455	0.064
Wet Sludge	0.009	*ND	0.065	*ND	0.002	0.004	0.001	0.158	0.082	0.011

Elements(ppm)	Co	Mn	Cr	V	Al	Be
Dry Sludge	0.003	0.295	0.075	0.022	4.536	*ND
Wet Sludge	0.001	0.058	0.014	0.003	0.75	*ND

* Not Detected . The Detection limit of the machine is 1ppb.

3.4.2 Brunauer-Emmett-Teller (BET) Surface Area Analysis

BET surface area of a given sample is analysed to determine the specific surface area -external surface area (macroporous and mesoporous) and microporous area- and pore size distribution. The result of this analysis can be employed to envisage the dissolution rate, as this rate is proportionally linked to the specific surface area.

The selected SDACs synthesized with two activation reagents ($ZnCl_2$ and KOH) were assessed for BET analysis. The BET instrument applied (Figure 3) by Particle Analytical (Micromeritics AS 3012, China) determines the specific surface area (m^2/g) of the samples. The samples were outgassed with a stream of dry non-reactive gas, (N_2) prior to the determination of the specific surface area to ensure a reliable measurement. The gas flow adsorption was very dynamic and certain flow of nitrogen gas was used as the adsorbate. Relative pressure (P/P_0) of 0.1, 0.2 and 0.3 were used as standard measurement points. The volume of gas adsorbed to the surface of the particles is measured at the boiling point of nitrogen (-196°C). The amount of adsorbed gas is correlated to the total surface area of the particles including pores in the surface and the calculation is based on the BET theory. Gas adsorption also enables the determination of size and volume distribution of micropores (0.35 – 2.0 nm).

The adsorption involved physical adsorption of gas (nitrogen) on the adsorbent's surface and subsequent calculation of the amount of trapped gas on the surface of the adsorbent equivalent to a monomolecular layer. The van der Waals forces were responsible for the physical adsorption of the gas on the adsorbent material.

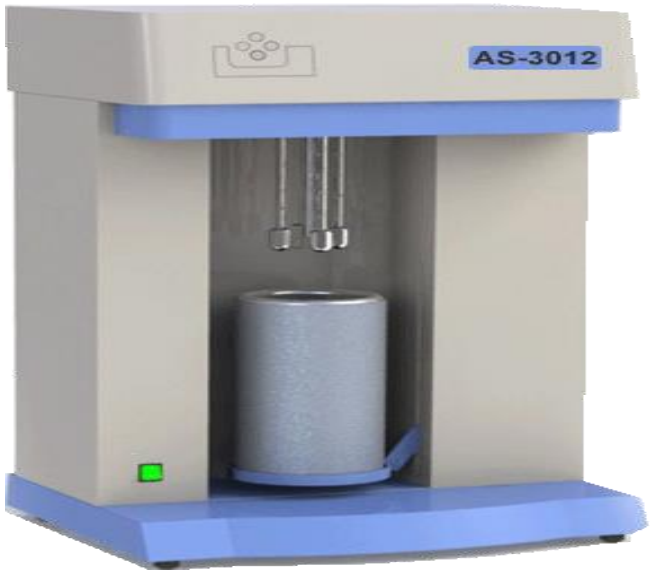

Figure 3 BET Surface Area Analyzer

3.4.3 Fourier Transform Infrared (FTIR) Spectroscopy Analysis

Fourier Transform Infrared (FT-IR) Spectroscopy is extensively used for both quantitative and qualitative analyses in almost all fields of Science. The technique operates on a core principle of irradiating the target specimen with a certain wavelength of electromagnetic radiation of the range 500cm^{-1} - 4000cm^{-1} (2500-20,000nm) to initiate the bending or stretching of the interplaying molecular bonds upon radiation absorption. The wavelength of the radiation absorbed is a characteristic of the bonds absorbing it. This technique is commonly used in Organic Chemistry and pharmaceutical companies for sample structural elucidation and impurities detection.

FTIR analysis was carried out to identify the functional groups in the original raw sludge and the SDACs. 2.5mg weight of each of the SDAC materials (3K-700-30, 2Z-700-90 2K-500-90, 2Z-500-30 and RAW) were mixed with KBr to 0.1 wt% and then pelletized. Thermo Nicole, FTIR (Madison, USA) (shown in Figure 4) was used to get the IR spectra of the samples. Transmittance data were collected for wavenumbers in the range of 500-4000cm^{-1}.

Figure 4 FT-IR (Thermo Nicole, FTIR (Madison, USA))

3.4.4 Thermo-Gravimetric Analysis (TGA)

Thermo-gravimetric concept operates on the underlying principle of measuring the weight loss or gain of a material with respect to a change in temperature. Solid state chemistry uses thermal analysis for studying reactions in the solid state, thermal degradation reactions, phase transitions and phase diagrams. In this experiment, the TGA of the selected adsorbent materials (based on GAC yield and BET surface area) were analyzed to assess their thermal capacity, mass changes, composition and kinetic parameters for a chemical reaction in the sample and coefficient of heat expansion. SDT Q600 TGA unit , shown in Figure 5, was employed for this work with about 7 – 10 mg of each of the four selected adsorbent material held on an alumina pan equipped with an excellent heat regulator (furnace thermo-element). A dynamic temperature ramped at 10 ^{0}C per minute to 900 ^{0}C and Argon gas with a flow rate of 100 mL per minute were adopted for this analysis.

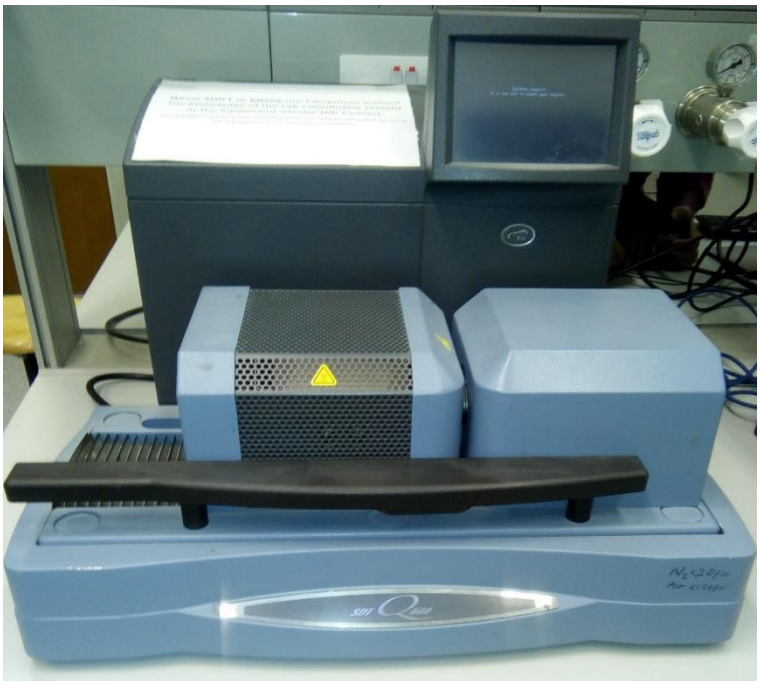

Figure 5 Thermogravimetric analyzer (SDT Q600 TGA)

3.4.5 Field Emission Scanning Electron Microscopy (FESEM)

Scanning Electron Microscope is a great and a highly sophisticated magnification machine that employs focused beams of highly energetic electrons to source detailed information about the target material. This machine provides three-dimensional images of high resolution that meet the needs of the modern day prodigious scientific stride in surface chemistry and petrochemical-based industries. It provides details of morphological, topographical and compositional data of any material by tracing it in a raster pattern with an electron beam.

For further characterization and a better understanding of the morphology and adsorption potentials of the prepared materials, field emission SEM analyses were carried out on them. The surface morphology of the samples was studied using SEM (JOEL JSM 5900LV) shown in Figure 6. To minimize the charging effect and at the same time achieve an enhanced visual appraisal of

the image, candidate samples were sputter-coated with a thin layer of gold prior analysis. Samples were set on stages (holders) and beams of electrons under a regulated voltage and network of associating lenses were focused on the samples. The acceleration rate of the incident electrons with significant kinetic energy determines the nature of surface-incident electron interaction. The reflected incident backscattered electrons detector (BSE) and secondary electron detector (SED) provide images that supply composition data related to the element and compound detection while the diffracted backscattered secondary electron (SE) imaging reveals the crystalline structure and mineral orientation of the sample. Directly above the sample and below the objective pole-piece was the high contrast BSE detector mounted, to achieve high-resolution micrographs at low kilovoltages (kV). The choice of FESEM was because it produces less electrostatically distorted clearer images with resolution as low as 1.5 nm. Although SEM is not as powerful and robust as its TEM counterpart in terms of image generation, the striking interactions of scanning electrons on the surface of the specimen and SEM's moderate magnification capacity (about 10nm) provide a greater field of view, high resolution and ultimately, a more detailed surface picture.

3.4.6 Microbiological Analysis of the sludge using SEM

Microbiological analysis was also undertaken to test the presence of microorganisms in the produced SDAC. Samples of 20mg each of the raw sludge and SDAC was measured into a 10ml plastic test tube containing a 10ml sterilised distilled water. Aliquots of 5ml each of the prepared inoculates was introduced into freshly prepared solid plate agar (solidified 0.8% agar-water solution) to grow colonies of microbes. They were then glued to the stub and coated with gold for examination in JEOL JSM-6460LV Scanning Electron Microscope (Bhatnagar et al., 2010; Oyehan and Al-Thukair, 2016).

3.4.7 Energy Dispersive X-ray Analysis (EDX)

The Energy Dispersive X-ray (EDX) Microscopy is a sister technique to SEM and is therefore always found coupled to it to acquire a better surface morphological analysis of the sample. The elemental composition of the SDAC was obtained from the SEM coupled with EDX (JSM 5800LV). A thin polymer window separates x-ray detector from the SEM chamber.

Figure 6 SEM Machine used for characterization (JOEL JSM 5800LV)

The detected x-ray's energy was determined by a pulse processing circuitry and the x-ray data was interpreted by an analyzer equipment before it was screened on the system. The x-ray detector is a lithium doped silicon semiconductor. When the sample was exposed to electrons of minimum kinetic energy, characteristic x-rays can be generated from it. This involves excitation of atoms in the sample by the incident electrons and during relaxation of the atoms, the transition of electrons from outer to inner electron shells result in the release of energy as photons. The x-ray detector is

a lithium doped silicon semiconductor. The striking of the semiconductor by the x-ray generated electrical charges, which were then analyzed to determine the number of x-rays emitted and their associated energy. The energy emissions were then used as fingerprints of the elemental composition of the samples of adsorbent materials. The surface morphological structure of all the sample states were analyzed by SEM-EDX (JOEL JSM 5800LV) shown in Figure 7.

Figure 7 SEM-EDX (JSM 5800LV)

3.5 DETERMINATION OF MTBE EQUILIBRIUM CONCENTRATION

MTBE is a hydrophilic organic compound with a very low Henry's constant of 0.024 and thus tends to dissolve more in water than in air and in any other media. To have a reliable assessment of the produced adsorbents' potentials for treating MTBE-contaminated aqueous solution and to ensure that the removal efficiency of MTBE was solely attributable to the adsorbents used, blank batch experimental runs were conducted to ascertain MTBE equilibrium concentration time. Prior

to this run, the whole stock of prepared MTBE solution (500ml of 1ppm MTBE) was stirred for 1 hour. Subsequently, ten 40ml-bottles (that covered 10 levels of the experiment) were filled to the brim with 40ml of 1ppm MTBE-spiked solution and the whole set up were left agitating on an isothermal shaker (Figure 8) for the chosen varied periods of time at a constant speed of 150rpm. Samples were taken at times 0, 1, 3, 5, 10, 27, 30, 60, 120 minutes and analyzed with GC-MS (Figure 9). The measured concentrations were plotted against time to determine the equilibrium concentration-time.

Figure 8 Mechanical shaker used for batch experiment

3.6 pH ZERO POINT OF CHARGE (pHpzc)

pHpzc describes the condition when the electrical charge density on the surface of the adsorbent is zero. It is usually determined in relation to an electrolyte's pH, and the pzc value is assigned to a given substrate, adsorbent or colloidal particle.

Batch equilibrium technique was employed to establish pHzpc of the SDAC powder. Certain portions of SDAC powder were introduced into a known volume (20ml) of 0.1mol/dm^3 KNO_3 solution. KNO_3 was selected as an inert electrolyte and the ionic strength was kept constant all along the experiments. Initial pH values (pH_i) of KNO_3 solution were adjusted from 3 to 11 by adding 0.1M HNO_3 or KOH. The set up was left to equilibrate for 24h in an isothermal shaker. The suspensions were filtered and the pH values (pH_f) were again measured using ion-pH meter(Tsyntsarski et al., 2013)

3.7 MTBE ADSORPTION BY SEWAGE SLUDGE DERIVED ACTIVATED CARBON (SDAC)

Deionized water was spiked with MTBE and was subsequently treated on a bench scale, using various dosages of the SDAC materials.

3.7.1 Preparation of MTBE Aqueous Solution

The stock MTBE solution used for this study was prepared from 99.999% purity (HPLC grade) MTBE standard solution purchased from Sigma-Aldrich. Deionized water from Mili-Q direct water purification system was used for dilution of the stock solution to the desired concentrations used in the batch experiments. The preparation process involved mixing appropriate volumes of

the MTBE with deionized water solution and stirring for 2 hours to ensure dissolution of the MTBE in water.

3.7.2 Batch MTBE Adsorption Experiments

A variety of pre-designed experiments were carried out using 40 mL of MTBE spiked deionized water. For each of the batch set up, different weights of the adsorbent material were added to the 40 mL spiked water containing a pre-determined concentration of MTBE and tightly sealed, to avoid loss by volatilization. The bottles were then placed on the isothermal shaker (Figure 10) at temperature of 25 ± 3^{o}C, while altering the experimental parameters, which included the agitation speed (50 – 200rpm), adsorbent dosage (0.5 – 4 g/L), contact time (15, 30, 60, 120 and 180mins), initial pH of solution (3 – 9), initial concentration of MTBE (500 – 4000 μg/L) and the type of adsorbent (SDAC and commercial activated carbon). After agitating the set up for a desired duration of time, the mixture was allowed to stand for 10minutes and 1mL of the sample was collected from the supernatant afterwards into a clean glass vial and analyzed using the GC/MS unit. For each of the batch experiments, blank runs were conducted to determine loss to the container/environment; and duplicate samples were also collected and analyzed as a form of quality control to ensure the accuracy of experimental results.

3.7.3 Chemical Analysis of MTBE

Following preparation of the stock solutions, the Thermo Scientific Trace GC Ultra gas chromatography/mass spectrometry (GC-MS) unit was calibrated to cover the range of concentrations to be used in the batch experiments (0.5 to 5,000 μg/L). For all of the concentration analyses, 1.0 mL of the solution was collected in a glass vial and analyzed.

The ISQ single quadrupole mass spectrometer coupled Thermo Scientific Trace Gas chromatography unit, fitted with a Triplus Headspace injector unit and an autosampler was used for the analysis of the MTBE concentrations in the samples collected during the batch experiments. A DB 520.2 fused silica capillary gas chromatography column was used in the unit (60 m – length; 0.32 mm – internal diameter and 1.80 μm thickness). The stationary phase used was diphenyl dimethyl polysiloxane, while the carrier gas was helium, at a constant flow rate of 1.7 mL/min. The instrument configuration was programmed at a temperature of 50 ^{0}C for 1 minute, ramped to 220^{0}C at the rate of 20^{0}C/min and held for 1 minute. In order to volatilize the target analyte, incubation of the sample bearing vials occurred at a temperature of 80^{0}C for 5 minutes in the auto-sampler, before the volatilized contents are taken by the syringe and injected into the unit. The electron ionization mode was utilized for the mass spectrometry unit (detector), having mass transfer line temperature of 200^{0}C and ion source temperature of 200^{0}C. Selected ion monitoring (SIM) mode was used to obtain the ion current at the mass to charge ratio of interest, having set the mass range of MTBE at 72.50 – 73.50. The amount of MTBE adsorbed per gram of adsorbent material (adsorption capacity (q_e)) and its percentage removal were as given in the equation below. The amount of adsorption at equilibrium, qe (mg/g), was calculated by:

$$q_e = \frac{(C_0 - C_e)V}{W} \qquad 1$$

$$\% \text{ Removal} = \frac{C_o - C_e}{C_o} \text{ x } 100\% \qquad 2$$

Where C_0 and C_e (mg/L) are the liquid-phase concentrations of dye at initial and equilibrium respectively. V is the volume of the solution (L) and W is the mass of dry adsorbent used (g).

Figure 9 Thermo Scientific Trace GC Ultra GC-MS

Figure 10 Solution-containing capped bottles on shaker

CHAPTER 4

RESULTS AND DISCUSSION

4.1. CHARACTERIZATION OF THE ADSORBENT MATERIALS

Characterizing the synthesized adsorbents, a sequel to the production process, was carried out to assess the surface morphology, interplaying functional groups, thermal stability, elemental composition and efficiency of the activation process. The outcomes of these characterizations were subsequently linked to the adsorption behavior of the synthesized adsorbents.

4.1.1. Brunauer-Emmett-Teller (BET) Surface Area Analysis

The BET total specific surface area in m^2/g of the adsorbent encompasses the external and microporous areas. This provides foresight to understanding the effects of the adsorbents' surface porosity and particle size distribution on the adsorption behavior. Table 13 shows the textural parameters of the selected adsorbent materials (3K-700-30, 2K-500-90, 2Z-500-30, and 2Z-700-90). The BET surface area of the adsorbents 3K-700-30, 2Z-700-90 2K-500-90, and 2Z-500-30, were respectively 450.99 m^2/g, 385.08 m^2/g, and 52.92 m^2/g. The 3K-700-30 has the highest BET surface area among the adsorbents. This is in line with the work of (Julcour Lebigue et al., 2010) who reported a larger surface area of 1686m^2/g with the same experimental conditions employed in this work but with a higher dwell time of 60 minutes. Pyrolysis, at 700^0C, irrespective of the time, generally increases the BET surface area as evident in this work where a significant increase in surface area was observed in 3K-700-30 and 2K-500-90 adsorbents. Both adsorbents were activated with the same reagent-KOH- but at a different temperature and reagent-solid ratio. This

was also supported by the previous works of Bagreev et al (Bagreev et al., 2001) where sewage sludges were pyrolyzed at various temperature ranges (400 - 950 ^{0}C) . A. Mendez et. (Méndez et al., 2013b), studied the physicochemical and agronomic properties of biochars synthesized from the sewage sludge, and reported a higher value of BET surface area for chemically activated sludge in comparison with the raw and other chemically activated sludge at lower temperatures. The combined effects of reagent's nature, impregnation ratio and dwell time are responsible for the relative difference in BET surface area analysis of both 3K-700-30 and 2Z-700-90. Although both samples were pyrolyzed at the same temperature, the respective applicable dwell times of 30 and 90 minutes are enough as plausible justifications for the variation in the BET surface area (Smith et al., 2009).

The porosity of any material can be assessed by conducting an adsorption isotherm experiment. Adsorption isotherm is a measure of the molar quantity of gas (say N_2) taken up (adsorped) or released (desorbed) at a constant temperature by an initially clean solid surface as a function of gas pressure . The test is usually conducted at a cryogenic temperature, typical of liquid nitrogen at its boiling point of 77.35K at one atmospheric pressure. A glance at the shape of the adsorption-desorption isotherm curve of a material tells a lot about its non-porous, microporous, mesoporous and macroporous nature (Molina-Sabio et al., 1995). Materials that have pores with openings less than 2nm (20 A^0), between 2 – 50 nm and greater than 50 nm are respectively said to be microporous, mesoporous and macroporous. Figure 11 shows the adsorption isotherms for N_2 at 77K determined for adsorbents 3K-700-30, 2K-500-90, 2Z-500-30, and 2Z-700-90. It can be generally observed that for all the four samples (except for 2Z-500-30), the quantity of N_2 adsorbed is low.

Table 13 Textural parameters obtained by N_2 adsorption isotherms of the adsorbents

Adsorbent	S_B	Se (m^2/g)		Sm (m^2/g)		Vt (cm^3/g)	Vm	Dp (A^0)
	(m^2/g)	% S_B		% S_B			(cm^3/g)	
RAW	1.54	1.47	95.64	0.07	4.36	0.00	Nil	0.00
3K-700-30	450.99	261.78	58.05	189.21	41.95	0.50	0.10	44.69
2K-500-90	52.92	44.75	84.56	8.17	15.44	0.09	0.07	80.83
2Z-700-90	385.08	171.71	44.59	213.37	55.41	0.36	0.12	37.52
2Z-500-30	37.80	21.76	57.67	16.00	42.33	0.05	0.01	48.45

S_B = BET surface area, Se = Mesoporous and macroporous size, Sm = Microporous size, Vt = Total pore volume, Vm = Micropores' volume, Dp = Average pore diameter.

However, the N_2 adsorption capacities of 3K-700-30, 2Z-500-30 and 2Z-700-90 were much larger compared to 2K-500-90 and raw sludge. In line with IUPAC classification, all adsorbents under comparison display isotherms that could be classified as type IV.A significant increase in N_2 adsorption was observed at high relative pressures (P/P^0) values between 0.9 and 1.0; an indicative of the presence of mesoporosity. The 0 A^0 value for the raw sludge is an indication of its non-porous nature. All adsorbents, as depicted in Table 13, are generally mesoporous in nature (pore sizes of 20 – 500 A^0) . The nascence of mesoporosity during activation is validated by the formation of hysteresis loops . Hysteresis loops are the resultant effects of the variation in the mechanisms of mesopore filling and emptying during capillary condensation and evaporation of adsorbing molecules respectively. As reported by many authors (Jindarom et al., 2007; S Rio et al., 2006), irrespective of pyrolysis conditions, all the solid products derived from sewage sludge pyrolysis were highly macroporous with relatively low mesopore and micropore area.

Figure 12 shows the plot of cumulative pore volume against pore diameter of 3K-700-30, 2K-500-90, 2Z-500-30, and 2Z-700-90.The similarity in the shapes of the three curves indicates that the pore size distribution did not undergo substantial change with pyrolysis temperature. The curves generally show an inverse relationship between the pore volumes and pore diameters of the produced adsorbents. A decrease in pore volume with increasing pore sizes was abrupt around 100A^0 until the curves relatively become constant at approximately 200A^0 pore size.

4.1.2. Characterization by Fourier Transform Infrared Spectroscopy (FTIR)

To identify the functional groups of the produced adsorbents, FT-IR spectroscopy was conducted. Figure 13 shows the FT-IR spectra for all the samples including the raw (3K-700-30, 2K-500-90, 2Z-500-30, 2Z-700-90 and RAW).

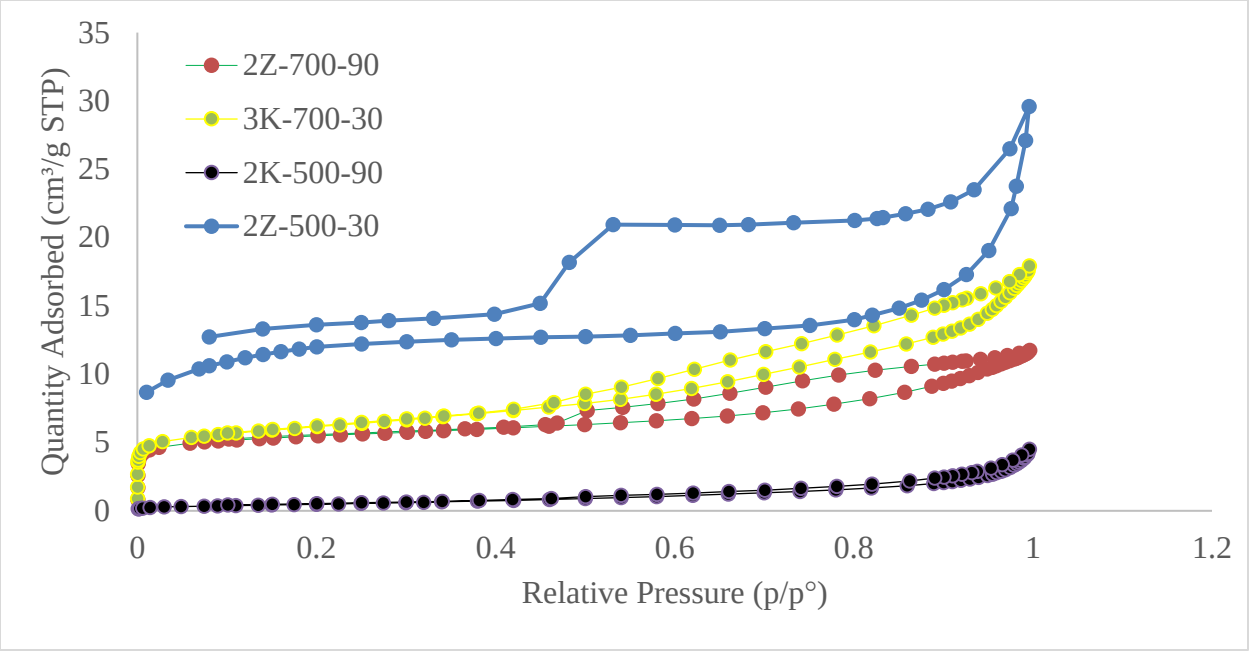

Figure 11 . Adsorption isotherms for N2 at 77K for the synthesized adsorbents

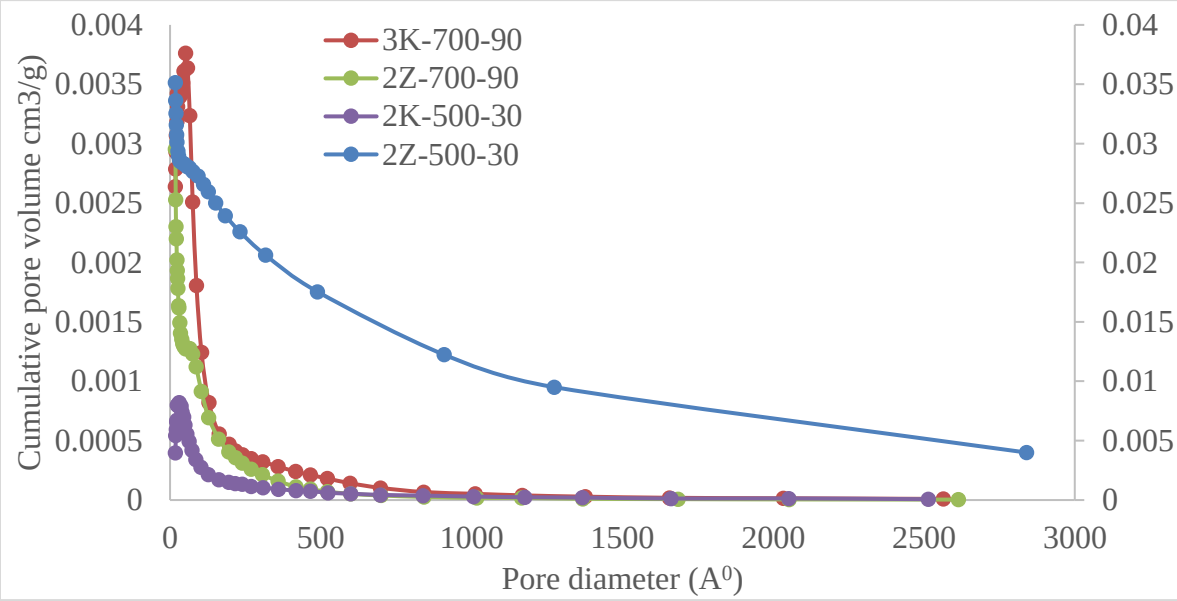

Figure 12 Cumulative pore volumes versus pore diameters of the synthesized adsorbents

The IR peaks observed for the raw at around 1080, 800 and 454 cm^{-1} can be respectively assigned to the asymmetric Si-O-Si stretch, the symmetric Si-O-Si, and the Si-O-Si deformation mode. Most of the bands observed in the raw sludge are very weak and are not distinctly conspicuous when compared to the 3K-700-30, 2K-500-90, 2Z-500-30, 2Z-700-90.

The surface structural changes in the solid matrix of the raw sludge are distinctly visible in the spectra of the other adsorbents. Peaks at 3550 and 1610 cm^{-1} in in the adsorbents correspond to stretching vibration of the hydroxyl groups, (Zou et al., 2013) (-OH or some chemically adsorbed water), and the surface adsorbed water or carboxylates (C=O) (Al-Qodah and Shawabkah, 2009; Zou et al., 2013). The two observed peaks around 3700 and 3600 cm^{-1} had also been attributed to the vibration of OH groups in the sludge (Hossain et al., 2011). The bands around 850 and 490 cm^{-1} for RAW are not as distinct as in the other adsorbents. This can be attributed to the bending modes of Si-O-Si (or Si-O-X, X=Fe, Al, Ca, Mg, and Na; or a blend of Si-O-Si and Si-O-X) in the RAW and Si-O-Si in the others. The observed bands in the RAW at 700-500 cm^{-1} can be linked to the vibration of the complex components. The structure of the raw sludge is expected to comprise blended framework of [SiO4] with some other impurities (like Al, Fe, Ca, Mg, Na etc.). Furthermore, in RAW, stretching vibration of C – H bond in aromatic structures is weakly shown at around 2924 cm^{-1} whereas, in the SDAC, this bond is almost invisible. The bands 2924 cm^{-1} (seen at 2954 cm^{-1} by Hossain et. al, (Hossain et al., 2011)) and 2847 cm^{-1} are respectively linked to aliphatic CH_3 asymmetric and symmetric stretching vibration. Based on these FTIR results, it can be concluded that SDAC has hydroxyl functional groups (-OH) that will enhance its adsorption capacity.

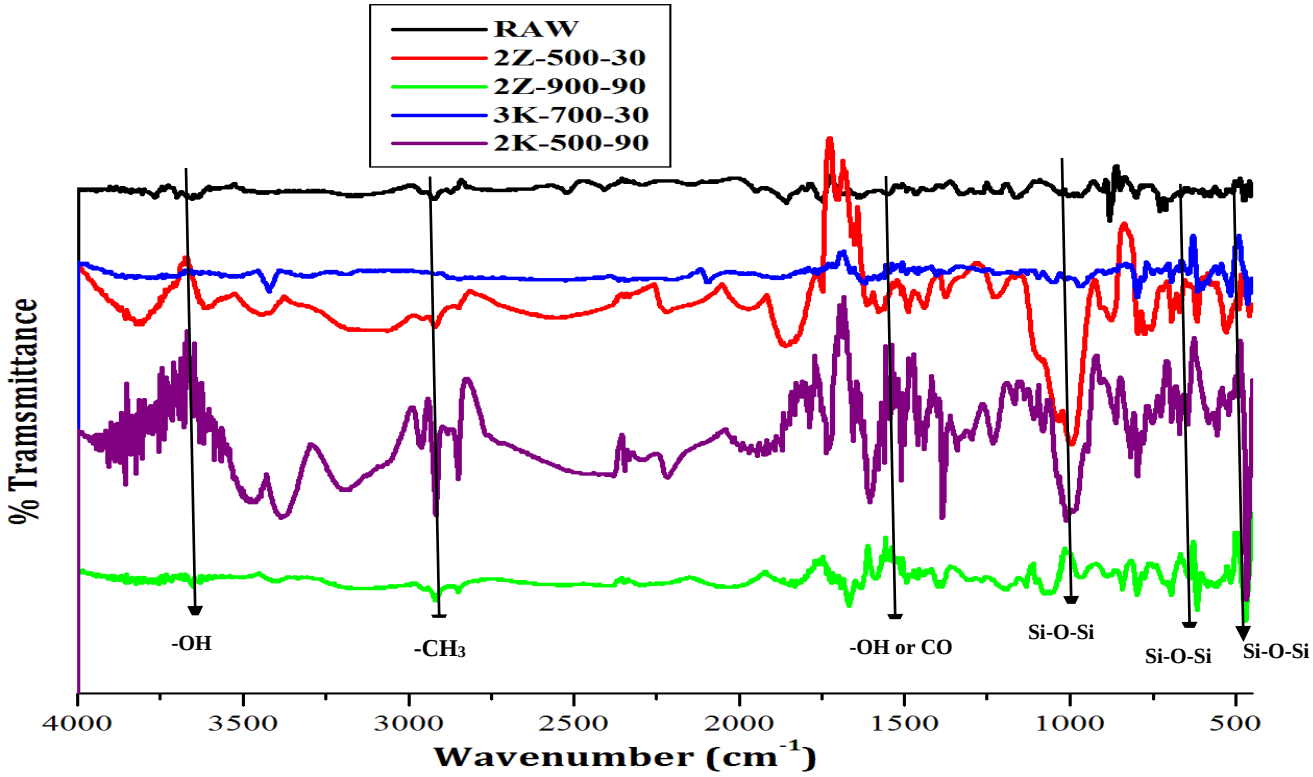

Figure 13 FT-IR peaks for adsorbents 3K-700-30, 2K-500-90, 2Z-500-30, 2Z-700-90 and RAW

4.1.3. Characterization by Thermo-Gravimetric Analysis (TGA)

Pyrolysis, as it was reported from the previous works (Martin et al., 2004; Otero et al., 2009), leads to carbonaceous residues that can be utilized as cheap carbon-based adsorbents. The qualities of the final residue depend on the experimental conditions and the employed raw materials' characteristics. During the pyrolysis of the sewage sludges in an inert system, significant physical and chemical changes in the states of organic matter occur (Lu et al., 2013). In consequence, weight differences due to the loss of light compounds, volatiles, less-thermally stabled compounds and the condensation/polymerization reactions take place. The most useful and interesting analytical technique that can be employed in characterizing various organic products such as sewage sludges (Méndez et al., 2005), pitches and other waste materials (Bagreev and Bandosz, 2002) is thermogravimetry. Previous thermogravimetric works have identified three main fractions in the

sewage sludge (Fang et al., 2010; Méndez et al., 2013a). The curve consists of small fraction of volatile components that were driven out around 29 – 110 ^{0}C, biodegradable materials that decomposed at temperatures lower than 300 ^{0}C and a large intermediate fractions related to the cellular organic polymers that are responsible for sludge biological stabilization (300 – 850 ^{0}C). Finally, the third main fractions that were thermally decomposed above 450 ^{0}C can be matched with the behavior of non-degradable materials.

Simultaneous TG-DSC analysis of the produced adsorbents (3K-700-30, 2K-500-90, 2Z-500-30, 2Z-700-90) is as displayed in Figure 14a. The exothermic peak at 29 – 110 ^{0}C for all the considered adsorbents (Figure 14b) and their associated weight losses (Table 14) was as shown. The weight losses at this temperature range can be attributed to the loss of adsorbed water from adsorbents. Weight losses at temperature range 110 – 300 ^{0}C can be attributed to the loss of biodegradables and other volatiles. As appeared in the TG-curve, the dramatic weight losses (>30%) in the range 300 - 850 ^{0}C as summarized in Table 14 is attributed to the decomposition/volatilization of organic and inorganic substance. According to the previous works(Méndez et al., 2013a; Zou et al., 2013), the most important weight loss is produced at temperatures range 300 to 850 ◦C, in all cases.

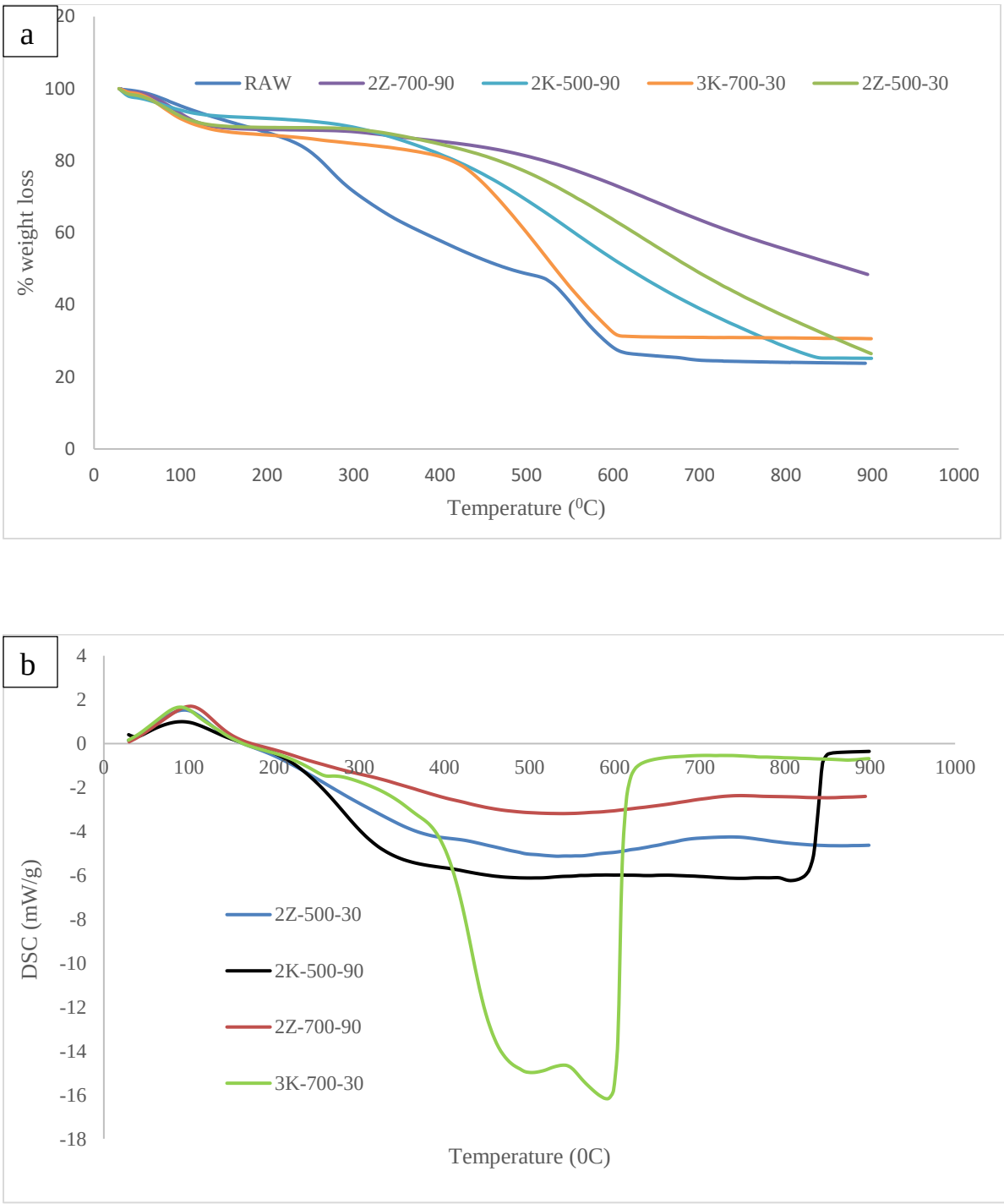

Figure 14 (a) TGA and (b) DSC analyses of SDACs

Table 14 Weight losses of SDACs at intermediate carbonization temperatures

Sample	***WL (%)**			
	29 – 110^{0}C	110 – 300^{0}C	300 – 850^{0}C	850 – 900^{0}C
2Z-700-90	9	3	32	0
2Z-500-30	6.4	3	59	0
3K-700-30	9	8	48	0
2K-500-90	6	4	63	0

*** Weight loss in percentage of the total weight.**

4.1.4. Characterization by Field Emission Scanning Electron Microscopy (FESEM)

To further understand the various changes in the mineral phases and surface morphology of the adsorbents in question and to assess the effect of acid washing in the production process, the scanning electron microscopy (SEM) images of the selected SDACs (both acid-washed and unwashed) were taken at different magnifications. The results are as shown in Figures 15 to 18. Figure 15 and Figure 17 shows SEM photographs of both acid-washed and unwashed SDACs taken at two different magnifications of 100kx and 50kx. Figure 15 shows images of the conspicuous, largely amorphous and granular particles of the acid-washed adsorbents with the dimension varied from 500 to 1000nm. On the other hand, Figure 16 and Figure 18 revealed the morphologies of unwashed pyrolyzed adsorbents to contain probably a wide range of minerals, organic matter, and probably some highly conjugated aromatic and aliphatic compounds which may be the main factors to the adsorbents' variation in surface charge and functional groups.

The risks involved in working with the municipal sewage sludge sourced from the wastewater treatment plant are immeasurable and can pose inimical health challenges to humans when not properly handled. Figure 19 shows some of the images of the culturing plates for SDAC and RAW. SDAC showed no microbial growth after the allowed incubation period (plate a) while the plate b with the RAW samples showed growths of Cocci (staphylococci, diplococci, streptococci) bacilli, spirilla, and vibrio Figure 20. The production process has successfully wiped out these microorganisms.

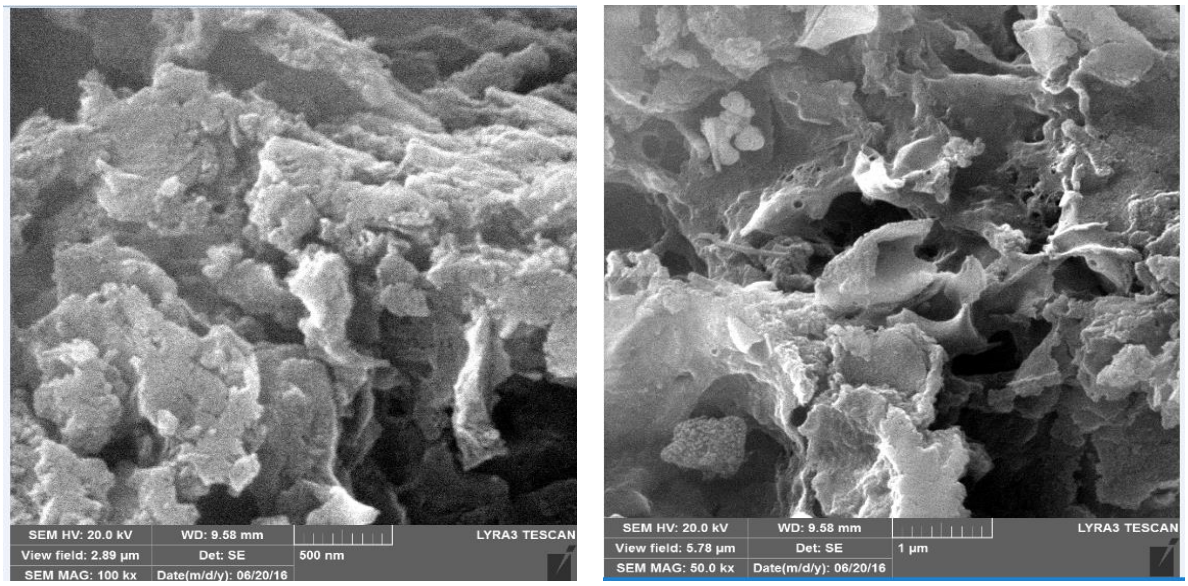

Figure 15 SEM micrograph of acid-washed 2K-500-90 (a) MAG 100kx (b) MAG 50kx

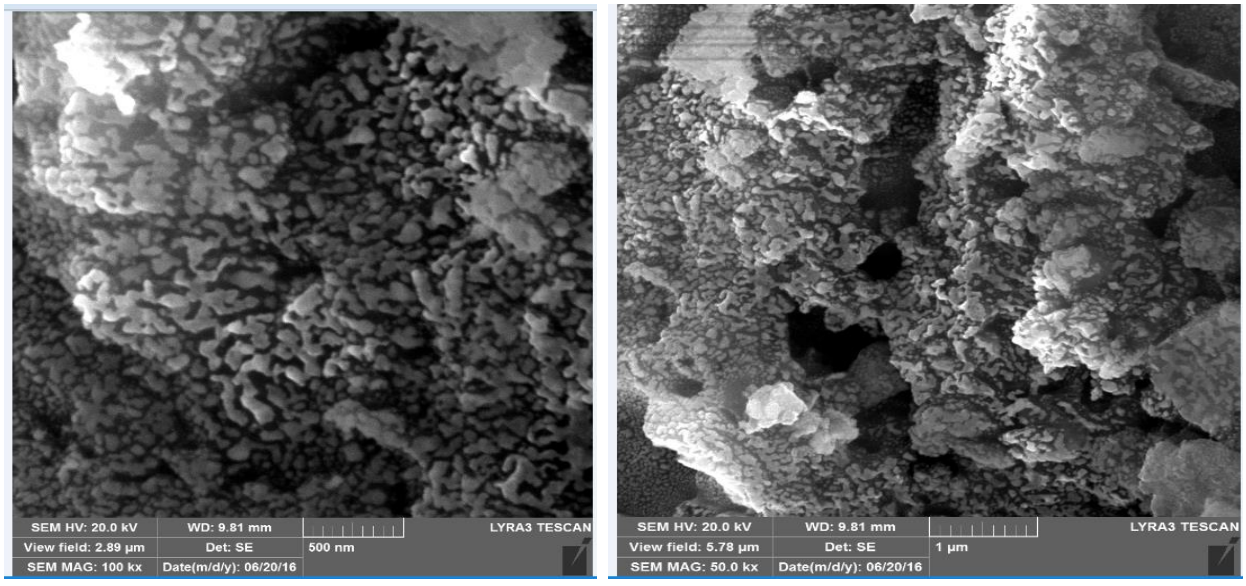

Figure 16 SEM micrograph of unwashed 2K-500-90 (a) MAG 100kx (b) MAG 50kx

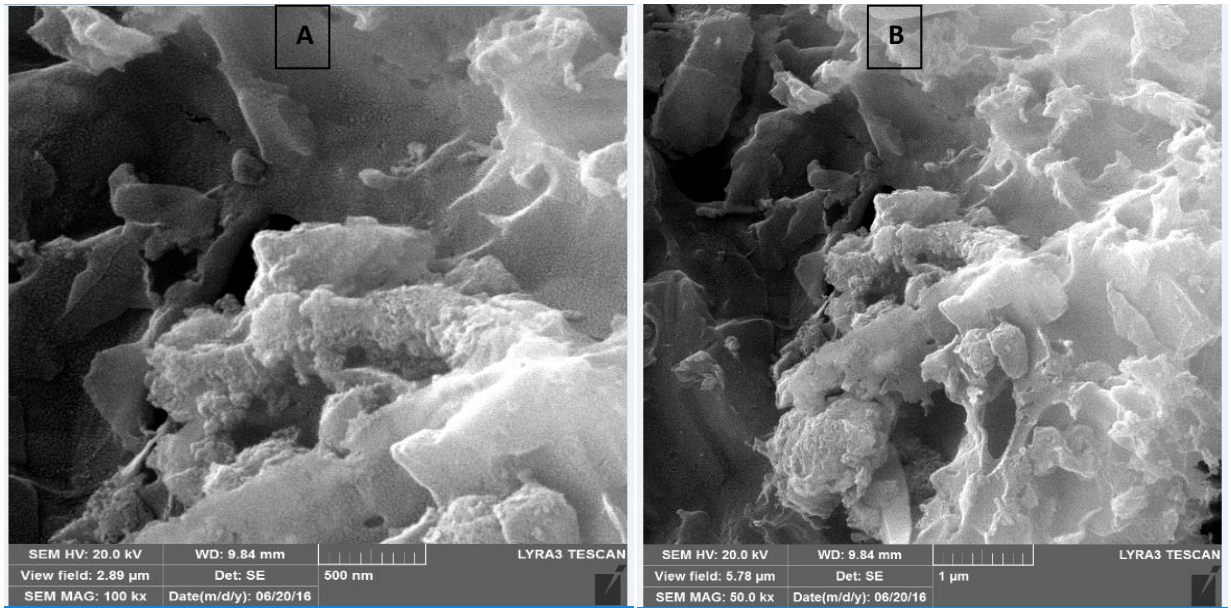

Figure 17. SEM micrograph of acid-washed 2Z-700-90 (a) MAG 100kx (b) MAG 50kx

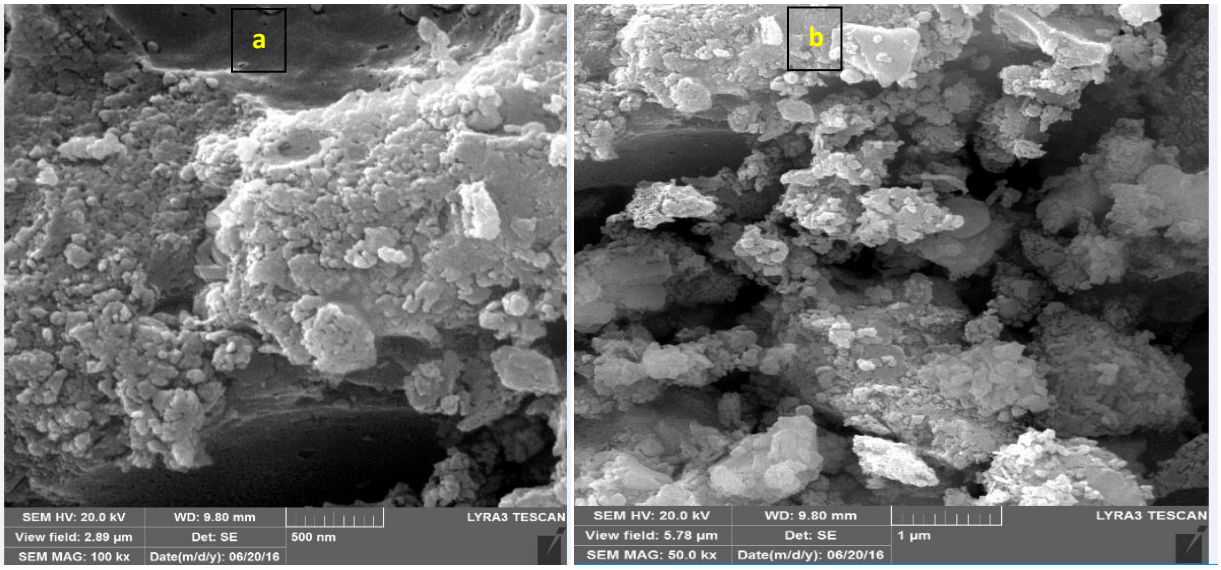

Figure 18. SEM micrograph of unwashed 2Z-700-90 (a) MAG 100kx (b) MAG 50kx

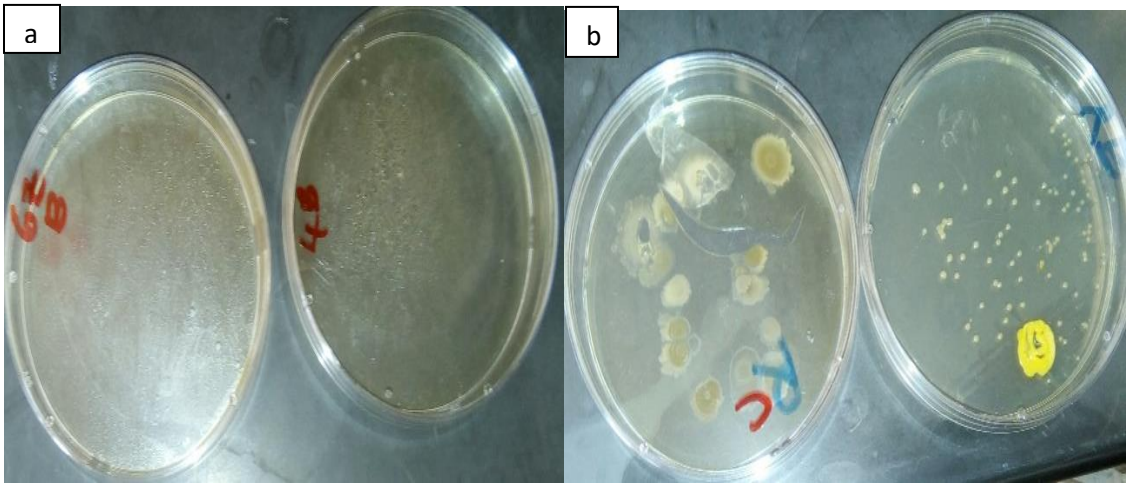

Figure 19. Images of the culturing plates for; (a)SDAC, (b)RAW

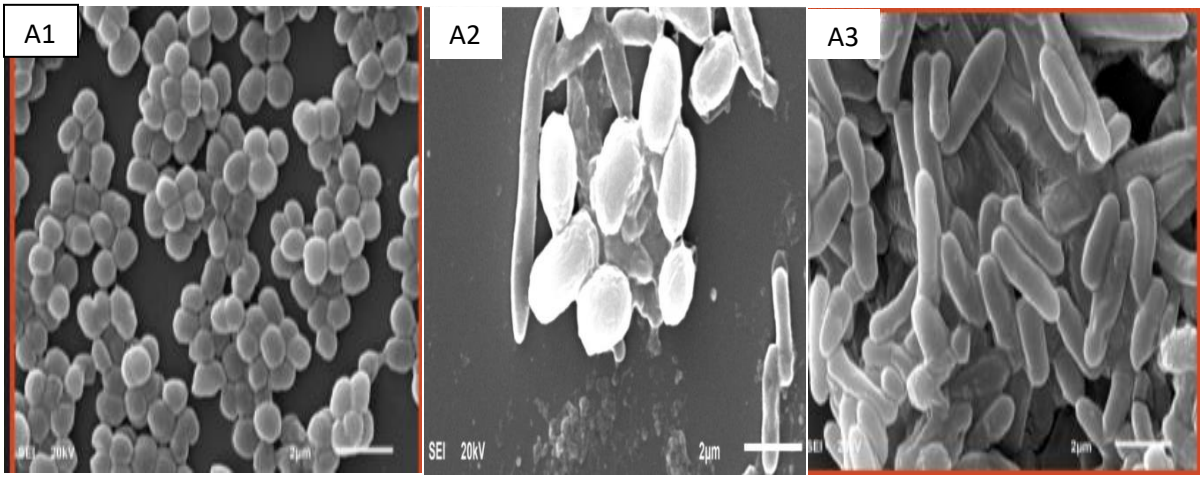

Figure 20. SEM micrographs of the RAW sludge

4.1.5. Energy Dispersive X-ray (EDX)

The elemental composition of the adsorbent materials (SDACs) and the real effect of acid-washing adopted in the production process are better understood by EDX spectroscopy. Figure 21 and Figure 22 showed the EDX spectra of both acid-washed and unwashed carbonaceous adsorbents of the SDACs representatives. EDX spectroscopy revealed the qualitative and quantitative measure of the existing metal impurities occurring in unwashed SDACs in form of elemental composition. Alkali and Alkali earth metals like K, Ca, Al, Mg, Zn, Fe, Si, and non-metallic elements like C, O, Cl, P, S were respectively found as feldspar, Wollastonite, bauxite, magnesium oxide, zinc metal, Iron, silica, limestone, potassium chloride, gallium phosphate and sulphates. The elements' respective abundances (represented in percentages by weight and by atom) are as presented in Figure 21. The effectiveness of washing the adsorbents with nitric acid was evident in the EDX spectra shown in the figure. Virtually all metals and non-metals impurities that can serve as potential sources of cross-contamination of the aqueous solution were significantly removed from the adsorbents with the exception of carbon, oxygen and scantily available silicon.

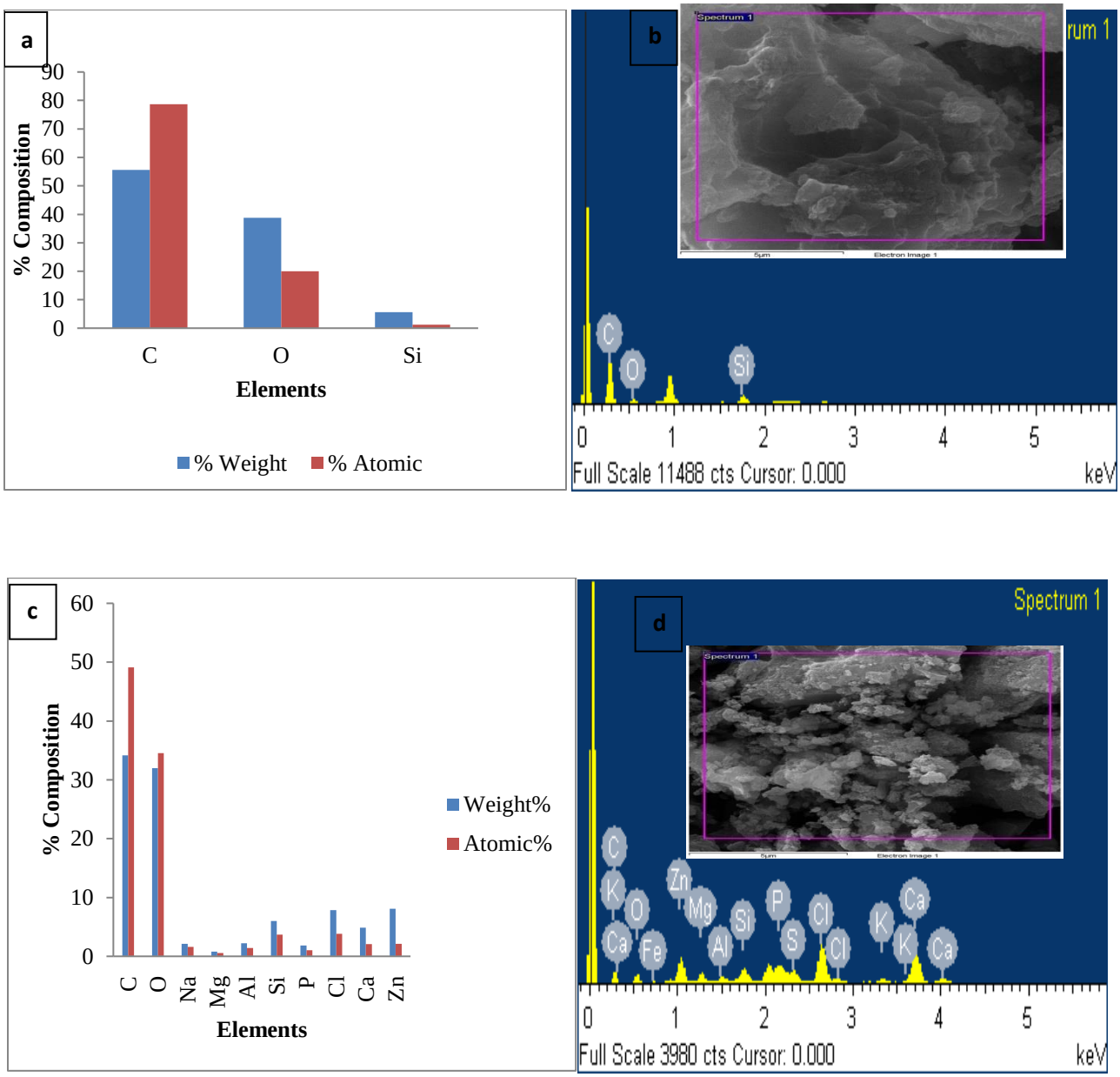

Figure 21. (a) % elemental composition of acid-treated 2Z-700-90 and (b) EDX micrograph of acid-treated 2Z-700-90 (c) % elemental composition of unwashed 2Z-700-90 and (d) EDX micrograph of unwashed 2Z-700-90.

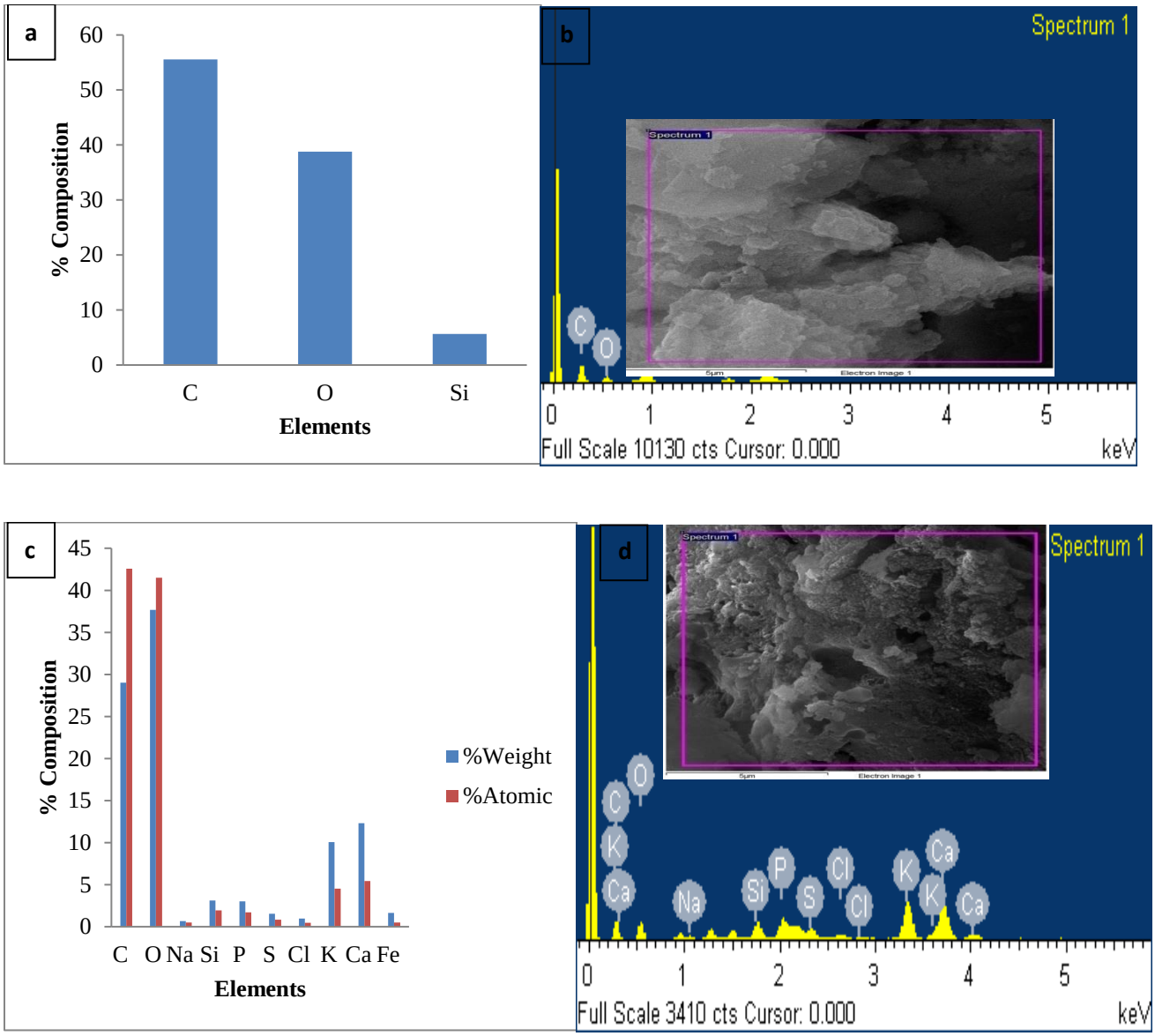

Figure 22. (a) % elemental composition of acid-washed 2K-500-90 and (b) EDX micrograph of acid-washed 2K-500-90 (c) % elemental composition of unwashed 2K-500-90 and (d) EDX micr graph of unwashed 2K-500-90

4.2. SELECTION OF THE ADSORBENT FOR MTBE ADSORPTION

Based on the combined qualities of GAC yield and BET surface area, adsorbent 2Z-700-90 is selected for MTBE removal. The report of BET surface area and GAC yield used for the selection is as shown in Table 15 and Figure 23. The quantity of adsorbents recovered after acid washing process is expressed as a percentage of the starting materials before washing so as to ascertain the respective yield of SDACs produced. The formula used to calculate the yield (Y) of the acid-washed adsorbents is:

$$Y = \frac{\text{the weight of the activated sludge after washing}}{\text{Weight of the activated sludge after pyrolysis}} \text{ x } 100\% \qquad 3$$

4.3 MTBE EQUILIBRIUM CONCENTRATION TIME RANGE DETERMINATION

In order to ensure that the documented removal of MTBE from the aqueous solution is solely attributable to the adsorbent utilized and at the same time determine the likely time of complete dissolution of MTBE in water, blank runs were conducted by agitating the MTBE-spiked aqueous solution over certain periods of time without adding the adsorbent. Figure 24 shows the curve of MTBE concentrations against time. A haphazard shape of the curve from time 0 to 10 minutes indicates a time when MTBE was dissolving. A nearly horizontal line style observed at time 27 to 60 minutes shows the insignificant variations in concentration of MTBE and thus represents a stage of complete dissolution of MTBE in the said MTBE-spiked aqueous solution. Continuous agitation beyond 60 minutes led to a decrease in the concentration of MTBE. The reduction in the concentration of MTBE in the aqueous medium may as a result of losses to the bottle container and environment via volatilization.

Table 15. Combined effects of BET surface area and GAC yield.

Appellation	BET S.A (m^2/g)	% GAC YIELD (GY)	BET X GY
2Z-500-30	37.8	53.4	20.2
2Z-700-90	385.1	68.0	261.9
3K-700-30	451.0	45.7	206.1
2K-500-90	52.9	46.8	24.8
RAW	6.8	Nill	

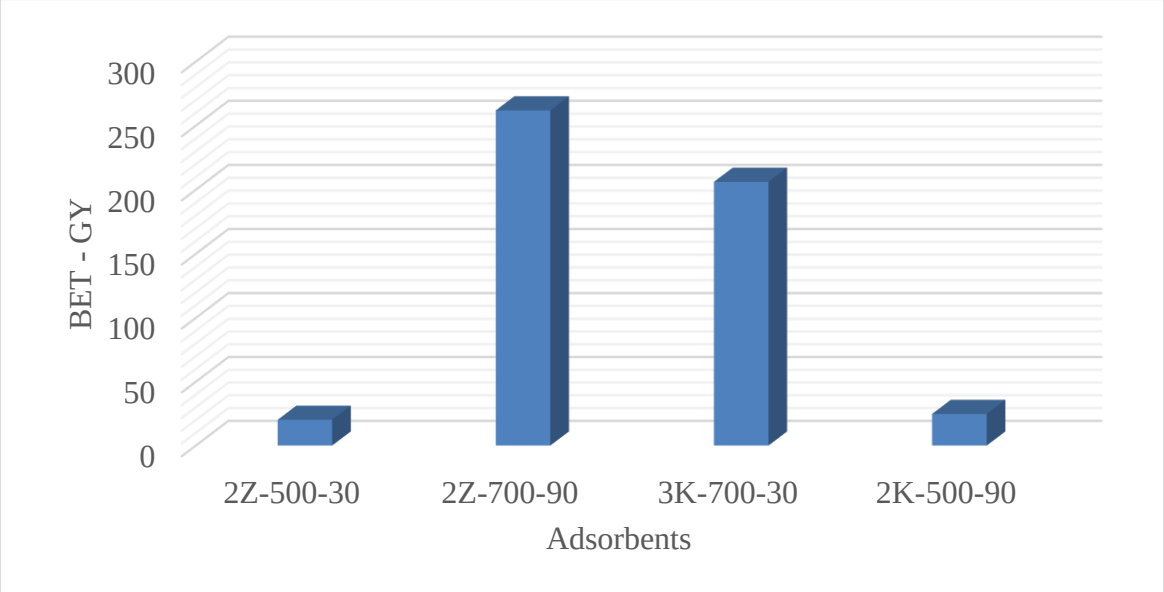

Figure 23. BET X GY values for different adsorbents produced

4.4. pH ZERO POINT OF CHARGE

One of the key determinants of the adsorbents' sorption potential for the target analyte is the surface charge distribution pattern. Generally, adsorbent's surface is either positively or negatively charged. The charge distribution pattern will be solely based on adsorbent-analyte surface interaction. In other words, a point or a state will be reached where adsorption will momentarily take place via microporous and mesoporous diffusion (Al-Qodah and Shawabkah, 2009). This state is called the surface zero point of charge (ZPC). If the pH of the solution is high enough, the surface becomes negatively charged and the positive ions from the solution (solute) will be attracted to the surface through electrostatic forces while the anions will be attracted at pH lower than the surface ZPC. Figure 25 shows the pHzpc of the adsorbent to be 7.16- a practically zero point of charge.

4.5. EFFECTS OF TREATMENT PARAMETERS ON MTBE REMOVAL

In order to identify the optimum treatment condition for the adsorption of MTBE using the selected the selected adsorbent 2Z-700-90, several experimental runs were conducted. The simultaneous comparative studies with the commercial activated carbon (CAC) were carried out for various treatment parameters such as adsorbate-adsorbent contact time, solution pH, initial adsorbate concentration, adsorbent dosage, and shaker's agitation speed. These studies were employed to ascertain the performance extents of the duo in MTBE removal and to assess the cost saved (in case the produced SDAC near or outperforms the CAC). In addition, the assessment of various treatment parameters for a batch experimental run is, among other objectives, to explore better MTBE adsorption capacity (and removal efficiency) of the selected adsorbent.

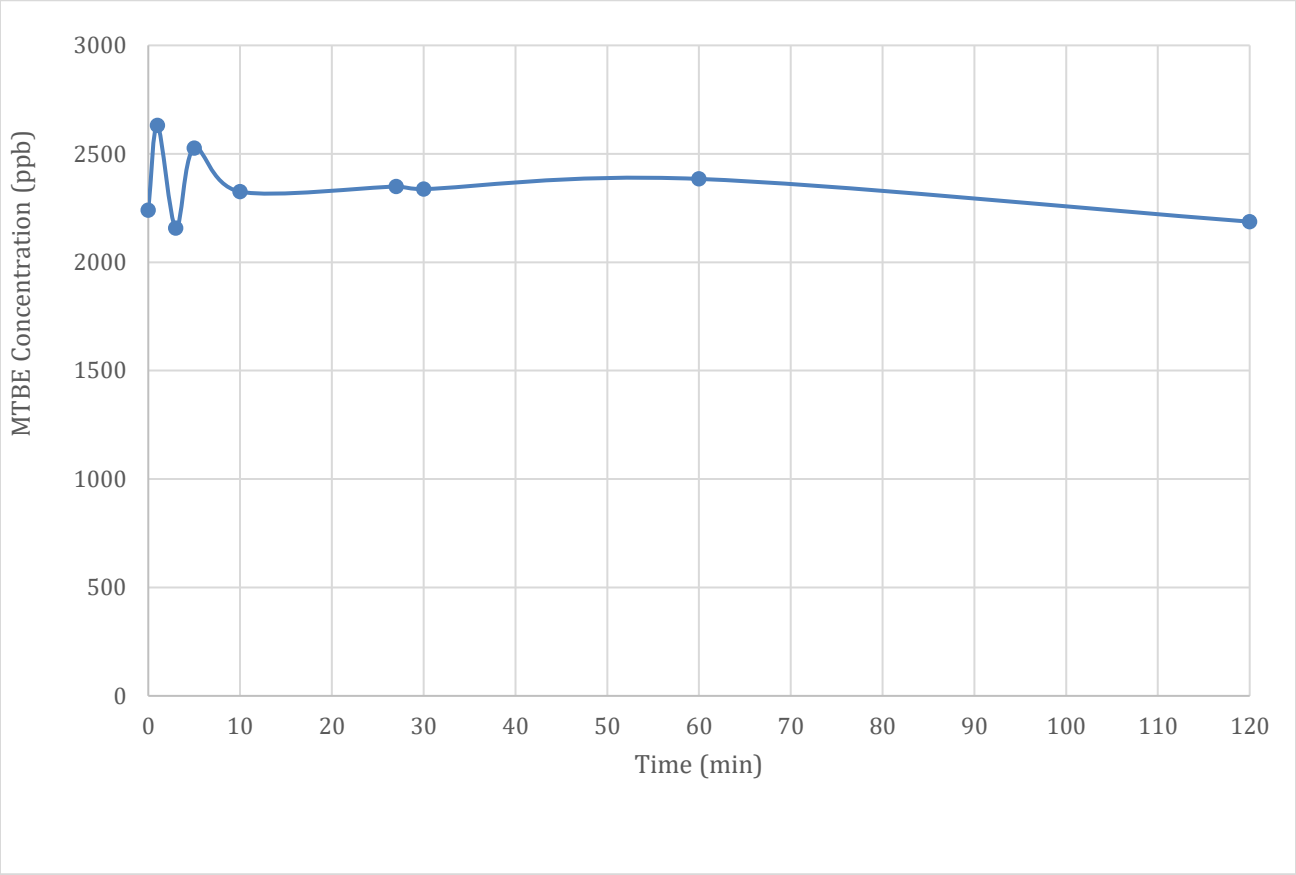

Figure 24. MTBE Blank run

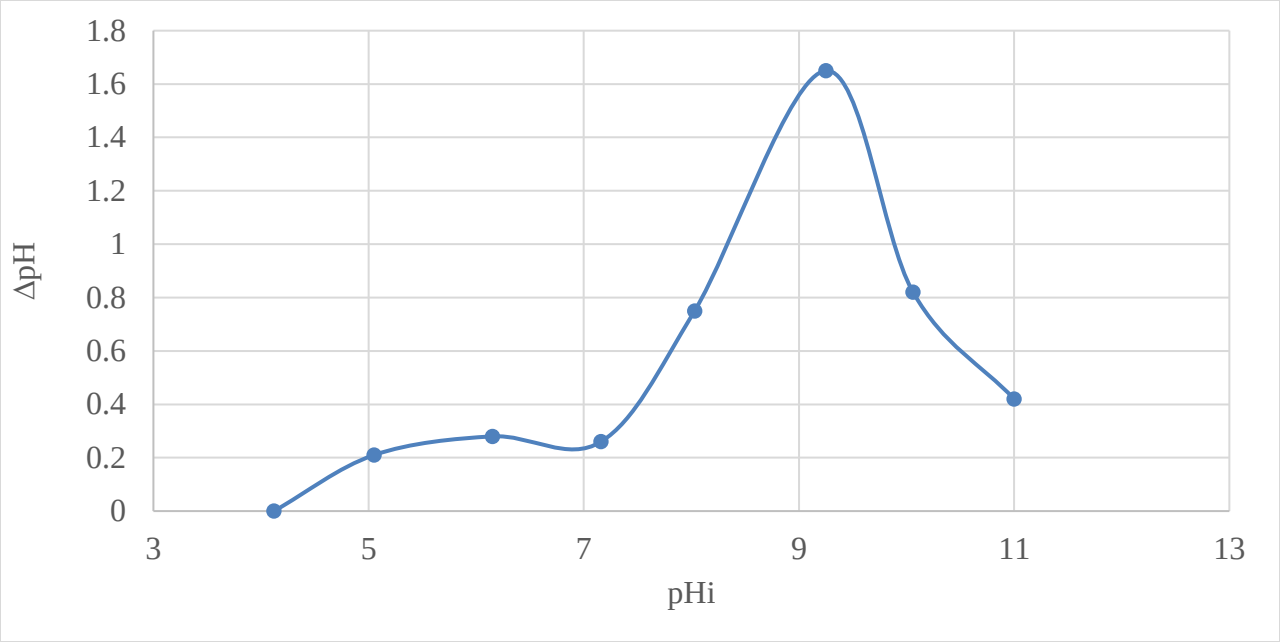

Figure 25. Zero point of charge of the SDAC

4.5.1. Effect of solution pH

The pH of the solution is the major factor utilized for controlling the adsorbent's surface charge and extent of ionization of the target analytes in solution. The adsorption of MTBE by the 2Z-700-90 and CAC at various pH values range (3-9) for the initial MTBE concentration of 1ppm, agitation speed of 150rpm, contact time of 60 minutes, constant room temperature and an adsorbent dosage of 2g/L was investigated. Figure 26 shows the adsorption behavior of 2Z-700-90compared to CAC at variable pH value ranges of 3 – 9. A remarkable variation in MTBE adsorption behavior under different variable conditions of pH was observed for the 2Z-700-90 and CAC. It is clear that the MTBE removal efficiency increases with increasing pH values until a peak was reached at around optimum contact time of 60 minutes after which the removal starts dropping down. Again, MTBE adsorptive behavior of the adsorbent in question was found to be optimum at pH 6 with a recorded MTBE removal efficiency of 45%. The MTBE removal efficiencies using CAC increased with increasing pH levels until a peak was reached in 60 minutes (with the exception of pH 3, 8 and 9 that reached their peak removal efficiencies at 120 minutes). The optimum pH range with the highest removal efficiency was found to be between 5 and 6 with a recorded removal of 65%. CAC at all levels of pH displayed a favorable and better adsorptive behavior for MTBE than SDAC (except at pH 6 where the latter outperforms the former). Eventually, pH 6 and initial contact time of 60 minutes were later fixed for the subsequent comparative studies of the two adsorbents.

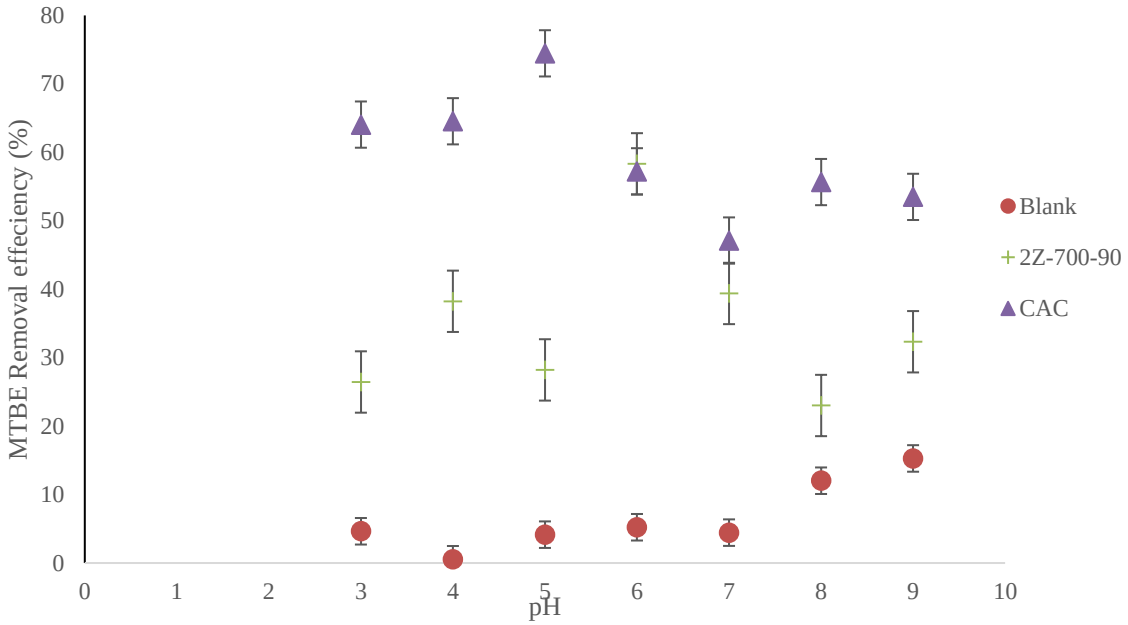

Figure 26. Effect of pH on MTBE removal by SDAC, CAC and blank

4.5.2 Effect of Contact Time

The effect of contact time in the adsorption process was also investigated. The adsorbent-adsorbate nature of interaction dictates the optimum contact time for the maximum removal efficiency (Rengaraj, 2002). The MTBE removal efficiency of 2Z-700-90 for different contact times was investigated. In the experiments, optimum pH of 6, initial MTBE concentration of 1ppm, adsorbent dosage rate of 2g/L and equilibrium time ranging from 30 min to 220 min were employed with a fixed agitation speed of 150rpm. The removal efficiency of MTBE by 2Z-700-90 and CAC was found to increase with time till 60 minutes of contact time after which there was a slight and gradual decline in the adsorption as shown in Figure 27. This observation can be explained by the

adsorption equilibrium phenomenon, in which the rate of adsorption was greater than the rate of desorption until the optimum contact time of 60 minutes, in which the adsorption sites on the adsorbent were saturated. Beyond this point, the rate of desorption was greater than the rate of adsorption, accounting for the slight and gradual decline in the MTBE adsorption beyond the optimum time of 60 minutes. Li *et al.* (Li et al., 2012) also reported 10% desorption upon the use of modified oil sludge (MOS) for MTBE removal from aqueous solution.

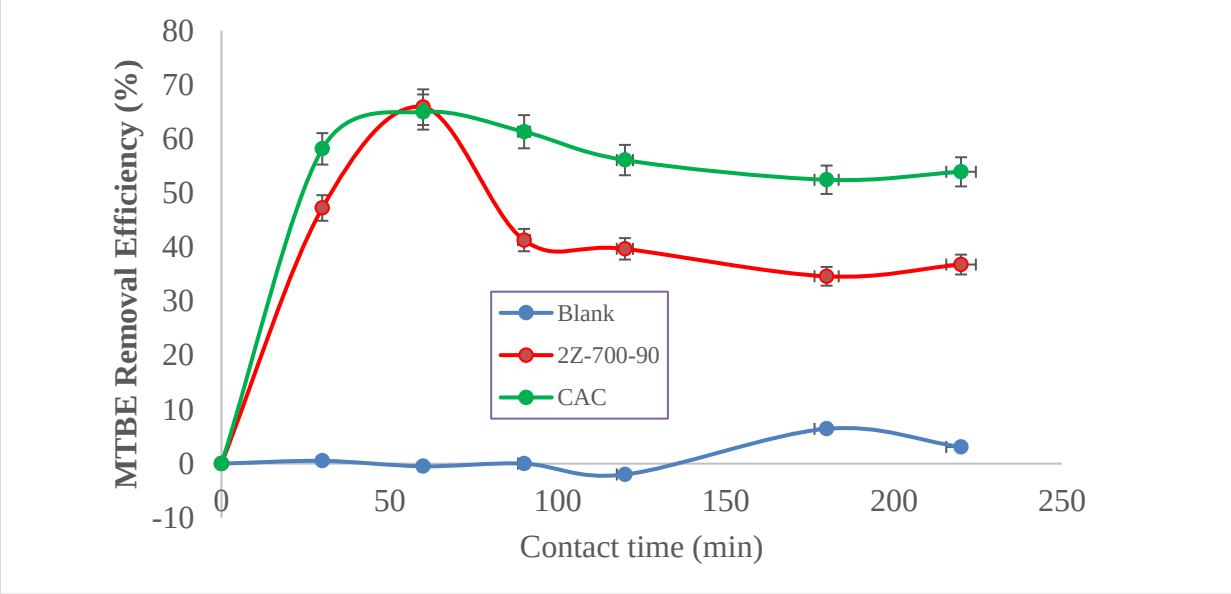

Figure 27. Effect of contact time on MTBE adsorption behavior of 2Z-700-90 and CAC

4.5.3 Effect of Adsorbent Dose

To study the impact of adsorbent dosage on the adsorption of MTBE, five different dosages (0.5, 1, 2, 3, 4g/l) each of SDAC and CAC were measured and assessed for their adsorption capacity and removal efficiency. The treatment parameters such as agitation speed, pH, time, temperature and initial concentration were respectively fixed at 150rpm, pH6, 60minutes, room temperature and 1ppm. In Figure 28, the removal efficiency of both adsorbents increased with increasing dosage rate. CAC's maximum removal efficiency of about 70% was reached at 1g/L dosage rate of the adsorbent and it was 35% more than that obtainable at the same 2Z-700-90 dosage rate. The availability of more binding sites owing to the increase in adsorption surface can be a plausible explanation for the increase in MTBE removal efficiency of both adsorbents. It can also be observed that the optimum removal efficiency (70%) for CAC and 2Z-700-90 were respectively reached at 1g/L and 2g/L. The increase in removal efficiency with increasing dosage rate of the adsorbent as observed in this work is in line with the previous works of (Rengaraj, 2002) that investigated the phenol removal efficiency of rubber seed coat, (Shah et al., 2015) who researched on iron impregnated activated carbon as an efficient adsorbent for the removal of Methylene Blue and much more recently Ganiyu et al (Ganiyu et al., 2016) studied the influence of aluminum impregnation on activated carbon for enhanced desulfurization of DBT at ambient temperature.

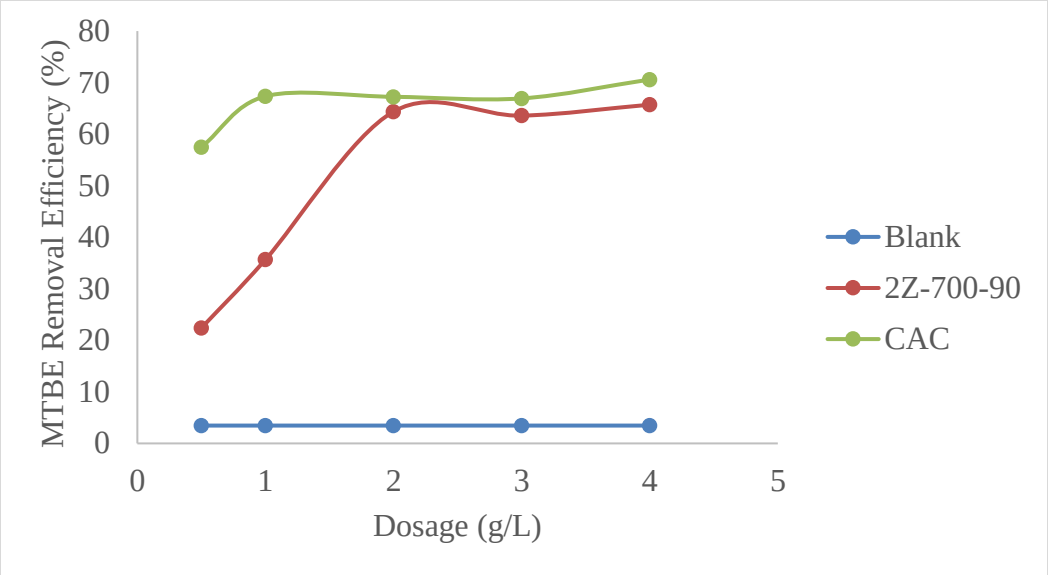

Figure 28. Effect of adsorbent dosage on MTBE adsorption behavior of CAC and 2Z-700-90

4.5.4 Effect of Initial MTBE Concentration

With respect to the nature of the adsorbent-adsorbate interaction, there is generally a decrease in the removal efficiency of both adsorbents with increasing adsorbate concentration. The decrease can be attributed to the saturation of the binding sites (adsorbing molecules) on the adsorbent (Salleh et al., 2011). This consequently culminates in a decreased surface area available for adsorption as the active sites on the surface of the adsorbent are occupied. This study, also, relatively shows the same trend for adsorption behavior of both adsorbents in question. Figure 29 summarizes the influence of initial concentrations of MTBE on the removal efficiencies and adsorptive capacities of the two adsorbents (2Z-700-90 and CAC) while fixing all other parameters. It can be observed that the highest obtainable removal efficiency for both adsorbents (57% for CAC and 51% for 2Z-700-90) was at the smallest concentration of 0.5ppm. The removal dropped gradually in CAC by 10% at 1ppm concentration and by 17% at other concentrations. Initial concentrations 0.5 and 1ppm seem favorable for adsorption in 2Z-700-90 also, as there was

a little drop in the removal from these two concentrations. The plausible explanation for this observation was that at low concentration, adsorbates have enough unsaturated active sites in the adsorbents to bind with and at higher concentrations when more and more of the adsorbates are available in the solution, the active bind sites receive the adsorbate until they reach the saturation point.

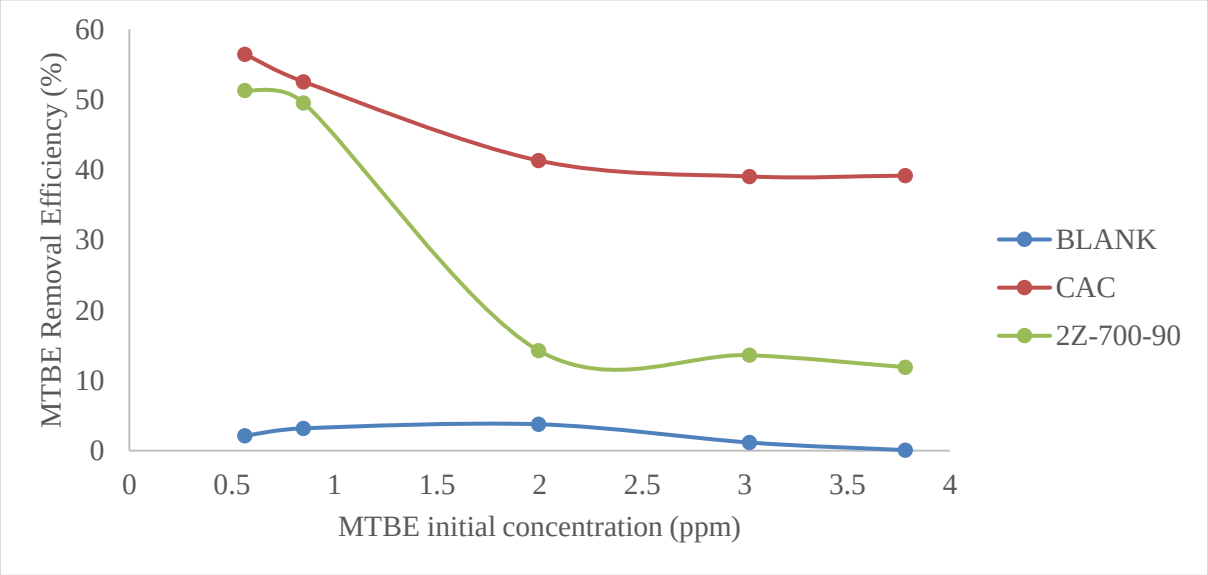

Figure 29. Effect of initial MTBE concentration on removal efficiency by CAC and 2Z-700-90

4.5.5 Effect of Agitation Speed

In adsorption experiment, the optimum time rate at which the adsorbate (MTBE in this case) comes in contact with active sites of the adsorbent is also germane to further understand the binding mechanisms of adsorbate with the adsorbent. Agitation speeds of the two extremities may not be favorable for effective adsorbate-adsorbent interactive binding. During the course of this comparative batch experiment for 2Z-700-90 and CAC, it was observed that the adsorbents precipitated at the bottom of the container while using the agitation speed of 50rpm, dispersed

slowly with an agitation speed of 100rpm, moderately with 150rpm and vigorously for 200rpm. The speed was however not increased beyond 200rpm to minimize MTBE loss through volatilization by the agitation process. Figure 30 aptly summarizes the results of the attainable MTBE removal efficiencies of both CAC and 2Z-700-90 under the employed agitation speeds. The curves of both adsorbents showed a similar trend and smaller removals of 3% and 15% were respectively recorded at agitation speeds 50 and 100rpm for 2Z-700-90. This may be attributable to the facts that the agitation speeds were not enough to create enough required contacts favorable for adsorption of MTBE (adsorbate) onto the surface of the adsorbents. In other words, agitation speeds of 50 and 100rpm were slightly able to trigger a smaller surface tension required for creating van der Waal's forces, covalent bonding or even electrostatic attraction. The observed dramatic increase in removal efficiency (50% for 2Z-700-90 and 60% for CAC) when the speed increased to 150rpm is attributable to the improved contact between the active adsorption sites on the adsorbent materials and MTBE in the solution that created the needed forces of attraction. The agitation speed of 200rpm was however too much as it was evident in a gradual drop in the removal efficiencies and adsorptive capacities of the two adsorbents. This may be attributed to the physical desorption of the adsorbents.

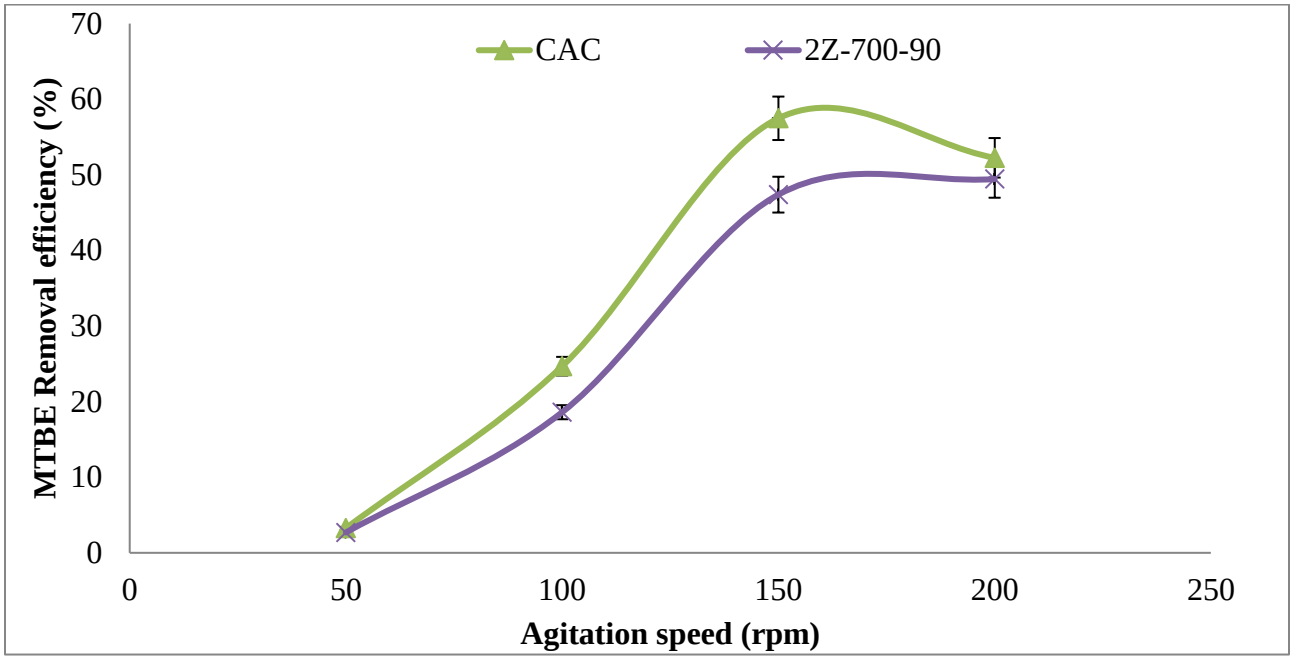

Figure 30. Effect of Agitation speed on MTBE adsorption behavior of the 2Z-700-90 and CAC

4.5.6 Effect of Temperature

To study the impact of temperature on the adsorption of MTBE, four different temperature ranges were selected for each of SDAC and CAC and assessed for their adsorption capacity and removal efficiency. The treatment parameters such as agitation speed, pH, time, dosage and initial concentration were respectively fixed at 150rpm, pH6, 60minutes, 4g/L and 1ppm.

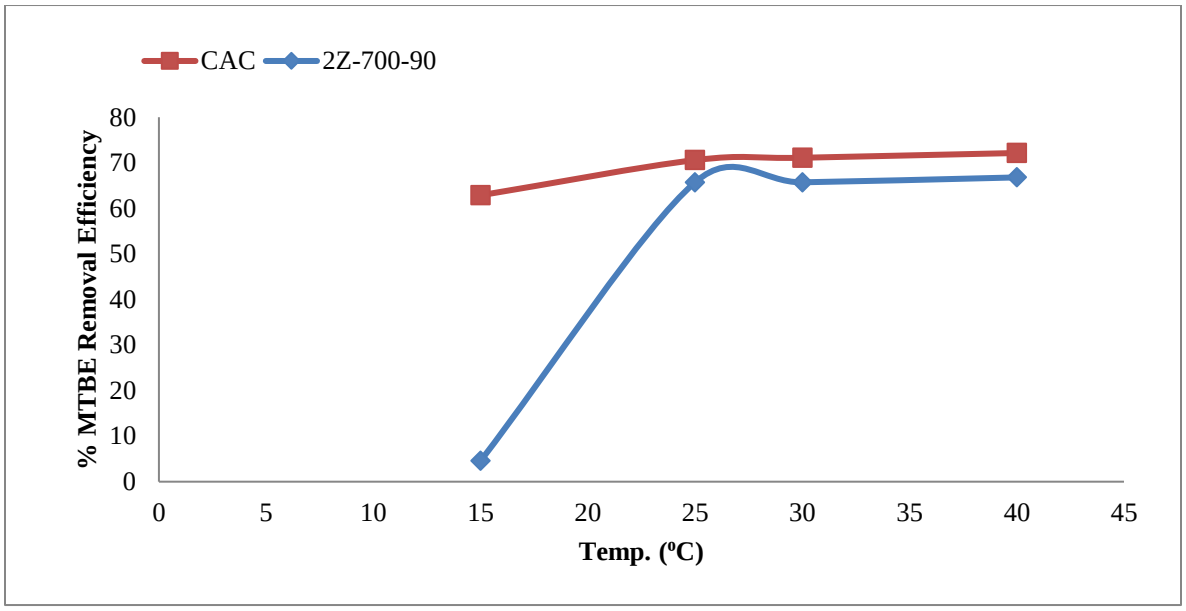

Figure 31. Effect of temperature on adsorption behaviour of CAC and 2Z-700-90.

Figure 31 summarizes the influence of temperature on MTBE removal efficiencies of the two adsorbents (SDAC and CAC) while fixing all other parameters. It can be observed from the levels of temperature employed that there was little influence on adsorption behavior of CAC. Higher removal of 60% was achieved even at 15 ^{0}C for CAC which later rose to 70% and got stabilized upon increasing the temperature points to 25, 35 and 40 ^{0}C. 2Z-700-90 adsorption behavior was

significantly affected by temperature. Lower pH of 15 ^{0}C and higher pH of 40 ^{0}C were unfavorable for adsorption. The adsorption of MTBE with SDAC favored room temperature

4.6. ADSORPTION ISOTHERMS

Adsorption isotherm' capacity is fundamental and plays a key role in determining the maximum removal efficiency, adsorbent's surface affinities for the target adsorbate, the mechanism of adsorption and the estimate of the adsorbent's economic viability when applied on a commercial scale for a particular solute (Senthil Kumar et al., 2010). The distribution of adsorbate molecule between the liquid phase and solid phase at the equilibrium state can be indicated by the adsorption isotherm. There are adequate models that can aptly describe the intended reaction mechanisms (such as equations of Langmuir, Freundlich, Redlich–Peterson, Koble–Corrigan, Sips, Toth, Temkin, and Dubinin–Radushkevich). However, Langmuir and Freundlich equations were adopted to assess the adsorption behavior of 2Z-700-90 for MTBE removal from the aqueous medium. The choice of 2Z-700-90 among all the adsorbents produced for MTBE removal was premised on the highest influenced of all by the combined effects of BET and GAC yield.

4.6.1 Langmuir Adsorption Isotherm

The Langmuir adsorption isotherm's theorem (Langmuir, 1916) is premised on the underlying hypothesis that the maximum obtainable adsorption will be reached when the adsorbent's surface attracts a saturated monolayer of solute molecules, the energy of adsorption is constant and there is no migration of adsorbate molecules in the surface plane. The existence of specific homogeneous sites within the adsorbent at which adsorption occurs is its main assumption. A nonlinear Langmuir equation is as expressed below:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (4)$$

Expressed in a linearized form:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{1}{q_m} C_e \quad (5)$$

Where: q_e is the adsorbed amount at equilibrium (mg/g), C_e is the concentration of adsorbate at equilibrium (mg/L), q_m is the maximum adsorption capacity and K_L is the Langmuir constant related to the energy of adsorption (Bhatnagar et al., 2010; Levchuk et al., 2014). q_m and K_L can be deduced from the slope and intercept by plotting $\frac{C_e}{q_e}$ againstC_e. The influence of adsorption isotherm shape can be discussed to judge the favorability of adsorption in terms of R_L a dimensionless constant of proportionality called separation factor or equilibrium parameter. R_L is defined by:

$$R_L = \frac{1}{1 + K_L C_0} \quad (6)$$

If R_L value is between 0 and 1,the adsorption is favorable and if RL is >1, =1 or = 0 the adsorption is respectively unfavorable, linear and irreversible (Paul et al., 2012)

4.6.2 Freundlich Isotherm models.

The Freundlich isotherm model was the second model applied in this study to explain the adsorption behavior of the adsorbent material. Adsorption on heterogeneous surfaces with the interaction between adsorbate molecules is the underlying hypothesis in the application of this model. It can further be stated that an exponential fall in adsorption energy upon completion of

adsorbents' sorption centers is the main assumption of this model (Crini and Badot, 2008). The Freundlich isotherm is expressed by the equation below:

$$q_e = K_f C_e^{1/n} \quad (7)$$

The above equation can be linearized in a convenient form by taking the logarithm of both sides as

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (8)$$

From the above equations, Ce is the equilibrium MTBE concentration (mg/L); qe is the amount of MTBE (mg) adsorbed per gram of the adsorbent at equilibrium (mg/g); K_f is the Freundlich adsorption constant related to the adsorbent adsorption capacity [(mg/g)(L/mg)1/n]. A linear plot of $\log q_e$ against $\log C_e$ was used to obtain the values of Kf and n from the intercept and slope respectively. Value of n should be in the range from 1 to 10 for favorable adsorption.

Adsorption isotherms of MTBE are presented in the Figure 32a and Figure 32b and the isotherm parameters for fitting Freundlich and Langmuir models are summarized in Table 16. From Table 16, Freundlich equation with correlation coefficient value of 0.9712 fitted the data for MTBE adsorption better than Langmuir's (0.9687) (Figure 32a and Figure 32b). Again, the amount of MTBE (in mg) adsorbed by 1g of 2Z-700-90 and MFA; (adsorption capacity) seemed to be the lowest among all other adsorbents compared in Table *16*.The respective adsorption capacities in mg/g for NNP, CMP, SDAC and MFA are 14.4, 2.18, 0.5 and 0.48. This suggests that our adsorbent's adsorption capacity needs to be improved upon.

Freundlich isotherm for MTBE adsorption assumes the exponential distribution of adsorption sites and energies and the multilayer adsorption of solute occurs on the heterogeneous surfaces

(Yu et al., 2005). This also justifies the results of the SEM images taken for the 2Z-700-90. The surface morphology of the adsorbent was revealed to be an amorphous, heterogeneous surface with relatively larger BET surface area.

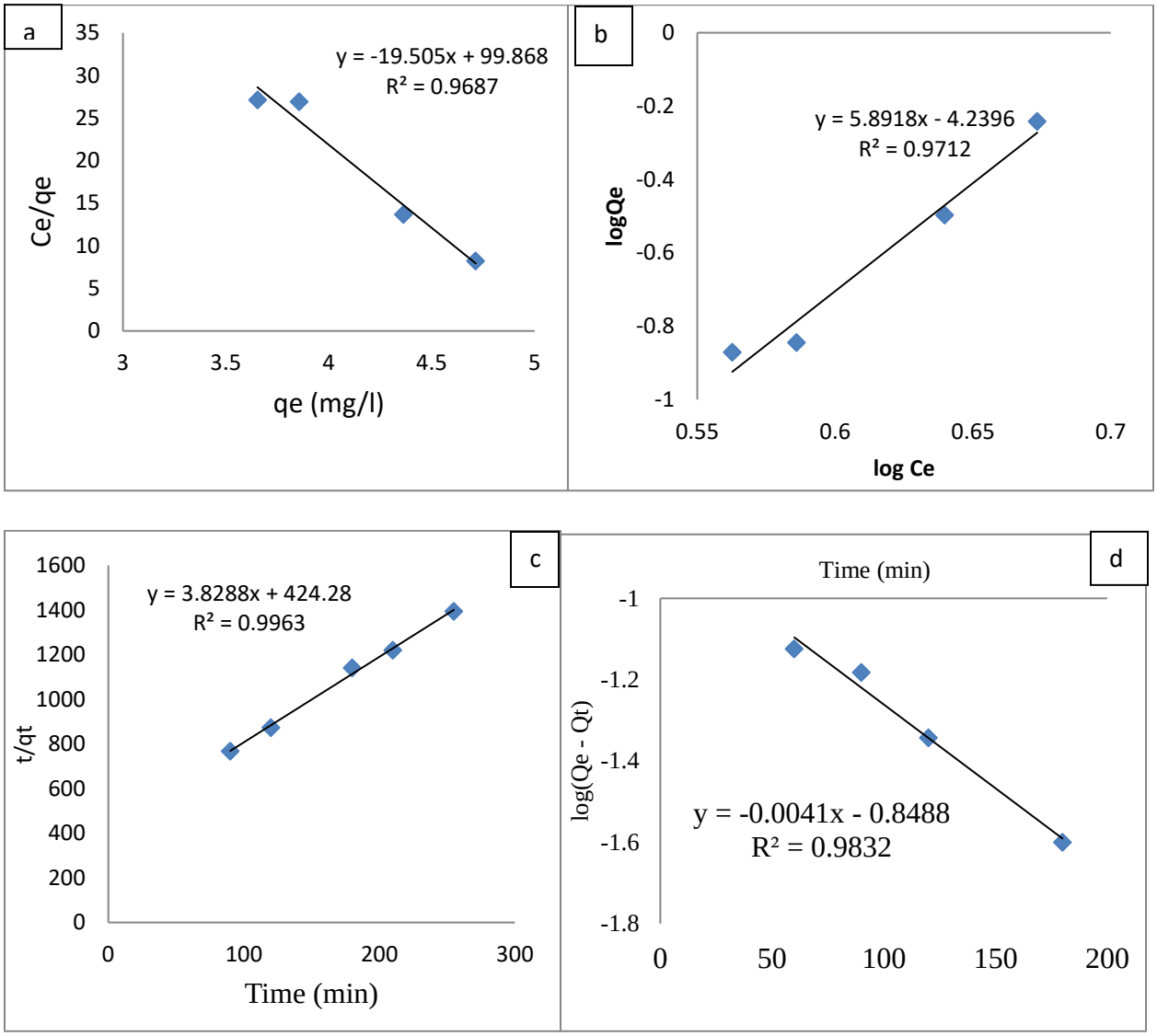

Figure 32 (a) Linearized Langmuir isotherms for MTBE adsorption; (b) Linearized Freundlich isotherms for MTBE adsorption; (c) pseudo-second-order sorption kinetics of MTBE; (d) pseudo-first-order sorption kinetics of MTBE.

Table 16. Freundlich & Langmuir adsorption isotherm of MTBE by 2Z-700-90 and other adsorbents

Solute	Adsorbent	Freundlich			Langmuir			Reference
		K_f	N	R^2	q_m (mg/g)	K_L (L mg^{-1})	R^2	
MTBE	[1]2Z-700-90	5.76E-5	0.1600	0.9712	0.0500	0.2005	0.9687	This work
MTBE	[2]MOS	231.8	1.23	0.93	NA	NA	NA	(Li et al., 2012)
MTBE	[3]MFA	0.514	17.83	0.783	0.48	-1.2472	0.9875	(Adebayo et al., 2016)
MTBE	[4]CMP	NA	NA	NA	2.18	0.118	0.9771	(Ji et al., 2009)
MTBE	[5]NPP	NA	NA	NA	14.8	0.076	0.9851	(Ji et al., 2009)

[1]Sewage Sludge-derived Activated Carbon, [2]Modified Oil sludge, [3]Modified Fly Ash, [4]Chromomethylated Polymer, [5]Non-polar Porous Polymer.

4.7 ADSORPTION KINETICS

Figure 32 shows a multiple linearized curves of the Langmuir and Freundlich isotherms for MTBE as well as the adsorption kinetics of the pseudo- first and pseudo-second-order reactions. The kinetic parameters of 2Z-700-90 are presented in Table 17. The correlation coefficient values (R^2) for both orders of reaction are above 0.97 and the fitting curves are all well linearized. The pseudo-first-order reaction's data are not available for the polymers (Chromomethylated Polymer; CMP, Non-porous Polar Polymer; NPP, and Postcrosslinked Polymer; PCP) compared with the 2Z-700-90 in Table 17. Of all the adsorbents compared, 2Z-700-90, though had the lower adsorption capacity, was the second in the list to have a faster adsorption rate constant of 3.52 x 10^{-2}g $mg^{-1}min^{-1}$ after chromomethylated polymer. This may be attributed to a moderate average pore width of the microporous size which allows MTBE to intra-diffusion.

Table 17. Kinetic parameters for adsorption of MTBE

Solute	Sample	pseudo-first-order			pseudo-second-order			
		q_e (mg/g)	K_1 (min^{-1})	R^2	q_e (mg/g)	K_2 (g mg^{-1} min^{-1})	R^2	Reference
MTBE	2Z-700-90	0.1416	9.44×10^{-3}	0.9832	0.26	3.52×10^{-2}	0.996	This work
	[1]CMP	NA	NA	NA	2.28	4.33×10^{-2}	0.999	(Ji et al., 2009)
	[2]NPP	NA	NA	NA	8.28	6.21×10^{-3}	1	(Ji et al., 2009)
	[3]PCP	NA	NA	NA	19.62	3.07×10^{-4}	0.998	(Ji et al., 2009)

[1]Chromomethylated Polymer, [2]Non-polar Porous Polymer. [3]Postcrosslinked Polymer.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1. CONCLUSION

This study focuses on producing the green adsorbent from bio-waste (sewage sludge). Sewage Sludge-derived Activated Carbon (SDAC) was synthesized, characterized and assessed for its Methyl Tert-Butyl Ether (MTBE) adsorption efficiency. The adsorbent produced was characterized, prior to exploring its potentials for MTBE removal, using FESEM, EDX, FTIR, TGA and BET. The results of the characterization suggest an amorphous mineralized material with a network of mediating -OH, -COOH, C=O, Si-O-Si as functioning group and a porous surface of $451 m^2/g$. Sludge derived adsorbent 2Z-700-90 was selected for adsorption, owing to its proven superseding characteristics of high yield and larger surface area. Comparative batch adsorption experiment was conducted using the commercial activated carbon (CAC) and 2Z-700-90. Removal efficiency of 70% was achieved by both adsorbents at the same experimental conditions but at different dosage rates of 2g/l of SDAC and 0.5g/l of CAC. The experimental data fitted better to the Freundlich Isotherm equation than Langmuir as revealed by R^2-values and followed the pseudo-second-order kinetics. This work demonstrated a beneficial use of a bio-waste such as sewage sludge in water decontamination technologies.

5.2. RECOMMENDATIONS

Despite that the fact that this study demonstrated a success in the use of SDAC for MTBE removal, there are still more issues that need further investigation. Some of these issues are:

1. Performing a continuous packed column adsorption study using SDAC.
2. Conducting the experiments at a pilot-scale level.
3. Other adsorbents' potential for MTBE removal efficiency can be explored.
4. Combined treatment methods such as oxidation-adsorption and bio-degradation-adsorption techniques using SDAC as adsorbent can be investigated for MTBE.
5. The options of impregnating and functionalizing the SDAC with polyelectrolyte to enhance adsorption can be a research gap to fill.
6. More adsorption isotherm equations can be explored to explain adsorption mechanisms of the SDAC.
7. The chemical reagents used for activation in this study were KOH and $ZnCl_2$. Other reagents such H_3PO_4, H_2SO_4, et.c can also be used.
8. The investigative adsorption study reported here can be extended for the dual and multiple solute analyses of the organic pollutants such as MTBE-BTEX.

REFERENCES

Ã, P.B.L.C., Young, T.M., 2000. Kinetics of Methyl Tert -Butyl Ether Degradation and By-Product Formation During Uv / Hydrogen Peroxide Water Treatment. Water Res. 34, 2233–2240.

Acero, J.L., Haderlein, S.B., Schmidt, T.C., Suter, M.J., von Gunten, U., 2001. MTBE oxidation by conventional ozonation and the combination ozone/hydrogen peroxide: efficiency of the processes and bromate formation. Environ. Sci. Technol. 35, 4252–9. doi:10.1021/es010044n

Adebayo, S.B., Tawabini, B.S., Atieh, M.A., Abuilaiwi, F.A., Alfadul, S., 2016. Investigating the removal of methyl tertiary butyl ether (MTBE) from water using raw and modified fly ash waste materials. Desalin. Water Treat. 3994, 19443994. doi:10.1080/19443994.2016.1172985

Ahmed, M.A., Diaz, C., Faaij, a, Gao, Q., Hashimoto, S., Mareckova, K., Pipatti, R., Zhang, T., Davidson, O.R., Bosch, P.R., Dave, R., 2007. Waste Management. Waste Manag. 27, 151–157. doi:10.1016/j.wasman.2010.08.009

Aktas, O., Cecen, F., 2007. Bioregeneration of activated carbon: a review. Int. Biodeterior. Biodegrad. 59, 257–272.

Al-Qodah, Z., Shawabkah, R., 2009. Production and characterization of granular activated carbon from activated sludge. Brazilian J. Chem. Eng. 26, 127–136. doi:10.1590/S0104-66322009000100012

An, Y., Kampbell, D.H., Cook, M.L., 2002. Co-Occurrence of MTBE and Benzene , Toluene , Ethylbenzene , and Xylene Compounds at Marinas in Large Reservoir 128, 902–906.

ATSDR, 1996. Toxicological profile for Methyl tert-butyl ether (MTBE). U.S. Dep. Heal. Hum. Serv. 268.

Bagreev, A., Bandosz, T.J., 2002. H2S adsorption/oxidation on materials obtained using sulfuric acid activation of sewage sludge-derived fertilizer. J. Colloid Interface Sci. 252, 188–194. doi:10.1006/jcis.2002.8419

Bagreev, A., Bandosz, T.J., Locke, D.C., 2001. Pore structure and surface chemistry of adsorbents obtained by pyrolysis of sewage sludge-derived fertilizer. Carbon N. Y. 39, 1971–1979. doi:10.1016/S0008-6223(01)00026-4

Bansal R. C., G.M., 2005. Activated carbon adsorption.

Bhatnagar, A., Kumar, E., Sillanpää, M., 2010. Nitrate removal from water by nano-alumina: Characterization and sorption studies. Chem. Eng. J. 163, 317–323. doi:10.1016/j.cej.2010.08.008

Bonjar, G.H., 2004. Potential ecotoxicological implication of methyl tert-butyl ether (MTBE) spills in the environment. Ecotoxicology 13, 631–635. doi:10.1007/s10646-003-4423-2

Bousba, S., Hassen, A., 2014. Removal of Phenol from Water by Adsorption onto Sewage Sludge Based Adsorbent 40, 235–240. doi:10.3303/CET1440040

Burbano, A.A., Dionysiou, D.D., Suidan, M.T., 2008. Effect of oxidant-to-substrate ratios on the degradation of MTBE with Fenton reagent. Water Res. 42, 3225–3239. doi:10.1016/j.watres.2008.04.004

Cassada, D. a, Zhang, Y., Snow, D.D., Spalding, R.F., 2000. Trace analysis of ethanol, MTBE, and related oxygenate compounds in water using solid-phase microextraction and gas chromatography/mass spectrometry. Anal. Chem. 72, 4654–4658. doi:10.1021/ac000462v

Che, G., Lakshmi, B.B., Martin, C.R., Fisher, E.R., 1999. Metal-Nanocluster-Filled Carbon Nanotubes: Catalytic Properties and Possible Applications in Electrochemical Energy Storage and Production. Langmuir 15, 750–758. doi:10.1021/la980663i

Chen, X., Jeyaseelan, S., Graham, N., 2002. Physical and chemical properties study of the activated carbon made from sewage sludge. Waste Manag. 22, 755–760. doi:10.1016/S0956-053X(02)00057-0

Chiang, P.C., You, J.H., 1987. Use of sewage sludge for manufacturing adsorbents. Can. J. Chem. Eng. 65, 922–927. doi:10.1002/cjce.5450650606

Crini, G., Badot, P.-M., 2008. Application of chitosan, a natural aminopolysaccharide, for dye removal from aqueous solutions by adsorption processes using batch studies: A review of recent literature. Prog. Polym. Sci. 33, 399–447. doi:10.1016/j.progpolymsci.2007.11.001

Dabrowski, A., Podkościelny, P., Hubicki, Z., Barczak, M., 2005. Adsorption of phenolic compounds by activated carbon--a critical review. Chemosphere 58, 1049–70. doi:10.1016/j.chemosphere.2004.09.067

Daifullah, A.A.M., Girgis, B.S., 1998. Removal of some substituted phenols by activated carbon obtained from agricultural waste. Water Res. 32, 1169–1177. doi:10.1016/S0043-1354(97)00310-2

Deeb, R.A., Scow, K.M., Alvarez-Cohen, L., 2000. Aerobic MTBE biodegradation: An examination of past studies, current challenges and future research directions. Biodegradation 11, 171–186. doi:10.1023/A:1011113320414

Delzer, G.C., Zogorski, J.S., Lopes, T.J., 1997. Occurrence of the gasoline oxygenate MTBE and BTEX compounds in municipal stormwater in the United States, 1991-95, Preprint Extended Abstracts. 213th ACS Natl. Meet. 37, No. 1, 374–376.

Dongmei Liab, Qin Liuab, Yi Gongab, Yufeng Huangc, X.H., 2009. Cytotoxicity and oxidative stress study in cultured rat Sertoli cells with Methyl tert-butyl ether (MTBE) exposure. Reprod. Toxicol. 27, 170–176. doi:10.1016/j.reprotox.2008.12.004

Fall, C., n.d. Activated Carbon from Sewage Sludge.

Fang, P., Cen, C., Chen, D., Tang, Z., 2010. Carbonaceous adsorbents prepared from sewage sludge and its application for Hg0 adsorption in simulated flue gas. Chinese J. Chem. Eng.

18, 231–238. doi:10.1016/S1004-9541(08)60347-X

Fitzmorris, K.B., Lima, I.M., Marshall, W.E., Reimers, R.S., 2006. Anion and Cation Leaching or Desorption from Activated Carbons from Municipal Sludge and Poultry Manure as Affected by pH. Water Environ. Res. 78, 2324–2329. doi:10.2175/106143006X95375

Ganiyu, S.A., Alhooshani, K., Sulaiman, K.O., Qamaruddin, M., Bakare, I.A., Tanimu, A., Saleh, T.A., 2016. Influence of aluminium impregnation on activated carbon for enhanced desulfurization of DBT at ambient temperature: Role of surface acidity and textural properties. Chem. Eng. J. 303, 489–500. doi:10.1016/j.cej.2016.06.005

Gascó, G., Méndez, A., Gascó, J.M., 2005. Preparation of carbon-based adsorbents from sewage sludge pyrolysis to remove metals from water. Desalination 180, 245–251. doi:10.1016/j.desal.2005.01.006

Goel, J., Kadirvelu, K., Rajagopal, C., Kumar Garg, V., 2005. Removal of lead(II) by adsorption using treated granular activated carbon: batch and column studies. J. Hazard. Mater. 125, 211–20. doi:10.1016/j.jhazmat.2005.05.032

Gu, L., Zhu, N., Guo, H., Huang, S., Lou, Z., Yuan, H., 2013. Adsorption and Fenton-like degradation of naphthalene dye intermediate on sewage sludge derived porous carbon. J. Hazard. Mater. 246–247, 145–53. doi:10.1016/j.jhazmat.2012.12.012

Hejazi, R.F., Husain, T., Khan, F.I., 2003. Landfarming operation of oily sludge in arid region—human health risk assessment. J. Hazard. Mater. 99, 287–302. doi:10.1016/S0304-3894(03)00062-1

Hong, J.Y., Yang, C.S., Lee, M., Wang, Y.Y., Huang, W.Q., Tan, Y., Patten, C.J., Bondoc, F.Y., 1997. Role of cytochromes P450 in the metabolism of methyl tert-butyl ether in human livers. Arch. Toxicol. 71, 266–269. doi:10.1007/s002040050386

Hossain, M.K., Strezov Vladimir, V., Chan, K.Y., Ziolkowski, A., Nelson, P.F., 2011. Influence of pyrolysis temperature on production and nutrient properties of wastewater sludge biochar. J. Environ. Manage. 92, 223–228. doi:10.1016/j.jenvman.2010.09.008

Inguanzo, M., Dominguez, A., Menendez, J.A., Blanco, C.G., Pis, J.J., 2002. On the Pyrolysis of Sewage Sludge: The Influence of Pyrolysis Temperature on Biochar, Liquid and Gas Fractions. J. Anal. Appl. Pyrolysis 63, 209–222. doi:10.4028/www.scientific.net/AMR.518-523.3412

Izrail S, Turovskiy, P.K.M., 2006. Wastewater Sludge Processing. Wiley, Florida.

Jaramillo, J., Álvarez, P.M., Gómez-Serrano, V., 2010. Oxidation of activated carbon by dry and wet methods. Fuel Process. Technol. 91, 1768–1775. doi:10.1016/j.fuproc.2010.07.018

Jarrah, R.T., Siddiqui, M.K., 2012. Sustainability: Opportunities and Challenges from a Construction Contractor's Perspective, in: ICSDEC 2012@sDeveloping the Frontier of Sustainable Design, Engineering, and Construction. ASCE, pp. 601–608.

Ji, B., Shao, F., Hu, G., Zheng, S., Zhang, Q., Xu, Z., 2009. Adsorption of methyl tert-butyl ether

(MTBE) from aqueous solution by porous polymeric adsorbents. J. Hazard. Mater. 161, 81–87. doi:10.1016/j.jhazmat.2008.03.052

Jindarom, C., Meeyoo, V., Kitiyanan, B., Rirksomboon, T., Rangsunvigit, P., 2007. Surface characterization and dye adsorptive capacities of char obtained from pyrolysis/gasification of sewage sludge. Chem. Eng. J. 133, 239–246. doi:10.1016/j.cej.2007.02.002

Julcour Lebigue, C., Andriantsiferana, C., N'Guessan Krou, Ayral, C., Mohamed, E., Wilhelm, A.M., Delmas, H., Le Coq, L., Gerente, C., Smith, K.M., Pullket, S., Fowler, G.D., Graham, N.J.D., 2010. Application of sludge-based carbonaceous materials in a hybrid water treatment process based on adsorption and catalytic wet air oxidation. J. Environ. Manage. 91, 2432–2439. doi:10.1016/j.jenvman.2010.06.008

Kane, S.R., Beller, H.R., Legler, T.C., Koester, C.J., Halden, R.U., Happel, A.M., 2001. Aerobic Biodegradation of Methyl tert -Butyl Ether by Aquifer Bacteria from Leaking Underground Storage Tank Sites Aerobic Biodegradation of Methyl tert -Butyl Ether by Aquifer Bacteria from Leaking Underground Storage Tank Sites. Am. Soc. Microbiol. 67, 5824–5829. doi:10.1128/AEM.67.12.5824

Kashi, A.M., Tahemanesh, K., Chaichian, S., Joghataei, M.T., Moradi, F., Tavangar, S.M., Najafabadi, A.S.M., Lotfibakhshaiesh, N., Beyranvand, S.P., Anvari-Yazdi, A.F., Abed, S.M., 2014. How to Prepare Biological Samples and Live Tissues for Scanning Electron Microscopy (SEM). Galen Med. J. 3, 63–80.

Kinner, N.E., Director, B.B.C., Salem, N.H., 2001. Fate, transport and remediation of MTBE. Testimony before US Senat. Comm. Environ. Public Work. Salem, NH. April 23.

Langmuir, I., 1916. the Constitution and Fundamental Properties of Solids and Liquids. Part I. Solids. J. Am. Chem. Soc. 252, 2221–2295. doi:10.1021/ja02268a002

Lenczewski, M., Leal-Bautista, R.M., Kroll, S.E., 2007. Influence of ethanol and methyl tert-butyl ether on the biodegradation and transport of benzene in loess. Environ. Geosci. 14, 137–148. doi:10.1306/eg.09150606006

Levchuk, I., Bhatnagar, A., Sillanpää, M., 2014. Overview of technologies for removal of methyl tert-butyl ether (MTBE) from water. Sci. Total Environ. 476–477, 415–433. doi:10.1016/j.scitotenv.2014.01.037

Li, Y., Liu, Y., Deng, H., Zhang, S., 2012. The Adsorption and Desorption Characteristics of a Novel Sorbent in Groundwater Remediation: Modified Oil Sludge. Adv. Mater. Res. 599, 412–417. doi:10.4028/www.scientific.net/AMR.599.412

Lien, H.-L., Wilkin, R., 2002. Reductive Activation of Dioxygen for Degradation of Methyl tert-Butyl Ether by Bifunctional Aluminum. Environ. Sci. Technol. 36, 4436–4440. doi:10.1021/es011449a

Lien, H.-L., Zhang, W.-X., 2007. Removal of methyl tert-butyl ether (MTBE) with Nafion. J. Hazard. Mater. 144, 194–199. doi:10.1016/j.jhazmat.2006.10.004

Lu, H., Zhang, W., Wang, S., Zhuang, L., Yang, Y., Qiu, R., 2013. Characterization of sewage

sludge-derived biochars from different feedstocks and pyrolysis temperatures. J. Anal. Appl. Pyrolysis 102, 137–143. doi:10.1016/j.jaap.2013.03.004

Martin, M.J., Artola, A., Balaguer, M.D., Rigola, M., 2002. Towards waste minimisation in WWTP: Activated carbon from biological sludge and its application in liquid phase adsorption. J. Chem. Technol. Biotechnol. 77, 825–833. doi:10.1002/jctb.645

Martin, M.J., Serra, E., Ros, A., Balaguer, M.D., Rigola, M., 2004. Carbonaceous adsorbents from sewage sludge and their application in a combined activated sludge-powdered activated carbon (AS-PAC) treatment. Carbon N. Y. 42, 1389–1394. doi:10.1016/j.carbon.2004.01.011

Méndez, A., Gascó, G., 2005. Optimization of water desalination using carbon-based adsorbents. Desalination 183, 249–255. doi:10.1016/j.desal.2005.03.038

Méndez, A., Gómez, A., Paz-Ferreiro, J., Gascó, G., 2012. Effects of sewage sludge biochar on plant metal availability after application to a Mediterranean soil. Chemosphere 89, 1354–1359. doi:10.1016/j.chemosphere.2012.05.092

Méndez, A., Tarquis, A.M., Saa-Requejo, A., Guerrero, F., Gascó, G., 2013a. Influence of pyrolysis temperature on composted sewage sludge biochar priming effect in a loamy soil, Chemosphere. doi:10.1016/j.chemosphere.2013.06.004

Méndez, A., Terradillos, M., Gascó, G., 2013b. Physicochemical and agronomic properties of biochar from sewage sludge pyrolysed at different temperatures. J. Anal. Appl. Pyrolysis 102, 124–130. doi:10.1016/j.jaap.2013.03.006

Méndez, a., Gascó, G., Freitas, M.M. a., Siebielec, G., Stuczynski, T., Figueiredo, J.L., 2005. Preparation of carbon-based adsorbents from pyrolysis and air activation of sewage sludges. Chem. Eng. J. 108, 169–177. doi:10.1016/j.cej.2005.01.015

Metcalf $Eddy, Inc., Tchobanoglous, G., Burton, F. L., Stensel, H.D., 2003. Wastewater Engineering, Treatment and Reuse. McGraw Hill Higher Education, New York.

Molina-Sabio, M., RodRíguez-Reinoso, F., Caturla, F., Sellés, M.J., 1995. Porosity in granular carbons activated with phosphoric acid. Carbon N. Y. 33, 1105–1113. doi:10.1016/0008-6223(95)00059-M

Moreels, D., Van Cauwenberghe, K., Debaere, B., Rurangwa, E., Vromant, N., Bastiaens, L., Diels, L., Springael, D., Merckx, R., Ollevier, F., 2006. Long-term exposure to environmentally relevant doses of methyl-tert-butyl ether causes significant reproductive dysfunction in the zebrafish (Danio rerio). Environ. Toxicol. Chem. 25, 2388–93.

Mrayyan, B., Battikhi, M.N., 2005. Biodegradation of total organic carbons (TOC) in Jordanian petroleum sludge. J. Hazard. Mater. 120, 127–134. doi:10.1016/j.jhazmat.2004.12.033

Otero, M., Rozada, F., Morán, A., Calvo, L.F., García, A.I., 2009. Removal of heavy metals from aqueous solution by sewage sludge based sorbents: competitive effects. Desalination 239, 46–57. doi:10.1016/j.desal.2008.03.005

Ouda, O.K.M., Raza, S.A., Al-Waked, R., Al-Asad, J.F., Nizami, A.-S., 2015. Waste-to-energy potential in the Western Province of Saudi Arabia. J. King Saud Univ. - Eng. Sci. doi:10.1016/j.jksues.2015.02.002

Oyehan, T.A., Al-Thukair, A.A., 2016. Isolation and characterization of PAH-degrading bacteria from the Eastern Province, Saudi Arabia. Mar. Pollut. Bull. doi:10.1016/j.marpolbul.2016.11.007

Pankow, J. , Korte, N., &Squillace, 1997. Review of the environmental behavior and fate of methyl tert-butyl ether.

Paul, M.L., Samuel, J., Das, S.B., Swaroop, S., Chandrasekaran, N., Mukherjee, A., 2012. Studies on Cr (VI) Removal from Aqueous Solutions by Nanoalumina. Ind. Eng. Chem. Res. 51, 15242–15250. doi:10.1021/ie302140a

Pietrzak, R., Bandosz, T.J., 2008. Interactions of NO2 with sewage sludge based composite adsorbents. J. Hazard. Mater. 154, 946–53. doi:10.1016/j.jhazmat.2007.10.109

Presidency of Meteorology and Environment, 2011. Ambient Water Quality Standards- Revised 13-04-2011 1–13.

Protection., O. of E.H.H.A.C.E., 2001. Public Health Goal for ALUMINUM.

Removals, 2007. The Production of Activated Carbons from Sewage Sludge 1–12.

Rengaraj, S., 2002. Removal of phenol from aqueous solution and resin manufacturing industry wastewater using an agricultural waste: rubber seed coat. J. Hazard. Mater. 89, 185–196. doi:10.1016/S0304-3894(01)00308-9

Reuter, J.E., Allen, B.C., Richards, R.C., Pankow, J.F., Goldman, C.R., Scholl, R.L., Seyfried, J.S., 1998. Concentrations, Sources, and Fate of the Gasoline Oxygenate Methyl tert -Butyl Ether (MTBE) in a Multiple-Use Lake. Environ. Sci. Technol. 32, 3666–3672. doi:10.1021/es9805223

Rio, S., Le Coq, L., Faur, C., Lecomte, D., Le Cloirec, P., 2006. Preparation of adsorbents from sewage sludge by steam activation for industrial emission treatment. Process Saf. Environ. Prot. 84, 258–264. doi:10.1205/psep.05161

Rio, S., Le Coq, L., Faur, C., Lecomte, D., Le Cloirec, P., 2006. Preparation of Adsorbents from Sewage Sludge by Steam Activation for Industrial Emission Treatment. Process Saf. Environ. Prot. 84, 258–264. doi:10.1205/psep.05161

Ros, A., Montes-Moran, M. a., Fuente, E., Nevskaia, D.M., Martin, M.J., 2006. Dried Sludges and Sludge-Based Chars for H_2S Removal at Low Temperature: Influence of Sewage Sludge Characteristics. Environ. Sci. Technol. 40, 302–309. doi:10.1021/es050996j

Ros, a., Lillo-Ródenas, M. a., Fuente, E., Montes-Morán, M. a., Martín, M.J., Linares-Solano, a., 2006. High surface area materials prepared from sewage sludge-based precursors. Chemosphere 65, 132–140. doi:10.1016/j.chemosphere.2006.02.017

Rossner, A., Knappe, D.R.U., 2008. MTBE adsorption on alternative adsorbents and packed bed adsorber performance. Water Res. 42, 2287–2299. doi:10.1016/j.watres.2007.12.009

Salleh, M.A.M., Mahmoud, D.K., Karim, W.A.W.A., Idris, A., 2011. Cationic and anionic dye adsorption by agricultural solid wastes: A comprehensive review. Desalination 280, 1–13. doi:10.1016/j.desal.2011.07.019

Senthil Kumar, P., Ramalingam, S., Senthamarai, C., Niranjanaa, M., Vijayalakshmi, P., Sivanesan, S., 2010. Adsorption of dye from aqueous solution by cashew nut shell: Studies on equilibrium isotherm, kinetics and thermodynamics of interactions. Desalination 261, 52–60. doi:10.1016/j.desal.2010.05.032

Shah, I., Adnan, R., Wan Ngah, W.S., Mohamed, N., 2015. Iron impregnated activated carbon as an efficient adsorbent for the removal of methylene blue: regeneration and kinetics studies. PLoS One 10, e0122603. doi:10.1371/journal.pone.0122603

Sheha, D., Khalaf, H., Daghestani, N., 2013. Experimental Design Methodology for the Preparation of Activated Carbon from Sewage Sludge by Chemical Activation Process. Arab. J. Sci. Eng. 38, 2941–2951. doi:10.1007/s13369-012-0470-4

Shih, T.C., Wangpaichitr, M., Suffet, M., 2003. Evaluation of granular activated carbon technology for the removal of methyl tertiary butyl ether (MTBE) from drinking water. Water Res. 37, 375–385. doi:10.1016/S0043-1354(02)00271-3

Smith, K.M., Fowler, G.D., Pullket, S., Graham, N.J.D., 2009. Sewage sludge-based adsorbents: a review of their production, properties and use in water treatment applications. Water Res. 43, 2569–94. doi:10.1016/j.watres.2009.02.038

Stefan, M.I., Mack, J., Bolton, J.R., 2000. Degradation Pathways during the Treatment of Methyl tert -Butyl Ether by the UV/H 2 O 2 Process. Environ. Sci. Technol. 34, 650–658. doi:10.1021/es9905748

Study, M.F., Nilsson, C., Dahlström, H., 2005. Treatment and Disposal Methods for Wastewater Sludge in the Area of Beijing , China. Environ. Eng.

Sublette, K.L., Snider, E.H., Sylvester, N.D., 1982. A review of the mechanism of powdered activated carbon enhancement of activated sludge treatment. Water Res. 16, 1075–1082.

Tawabini, B., Zubair, A., 2011. Bromate control in phenol-contaminated water treated by UV and ozone processes. Desalination 267, 16–19. doi:10.1016/j.desal.2010.08.039

Tawabini, B.S., 2014. Simultaneous removal of MTBE and benzene from contaminated groundwater using ultraviolet-based ozone and hydrogen peroxide. Int. J. Photoenergy 2014. doi:10.1155/2014/452356

Tsyntsarski, B., Marinov, S., Budinova, T., Yardim, M.F., Petrov, N., 2013. Synthesis and characterization of activated carbon from natural asphaltites. Fuel Process. Technol. 116, 346–349. doi:10.1016/j.fuproc.2013.07.020

U. S. Environmental ProtectionAgency., 1979. Process Design Manual for Sludge Treatment and

Disposal.

Uggetti, E., Ferrer, I., Llorens, E., García, J., 2010. Sludge treatment wetlands: A review on the state of the art. Bioresour. Technol. 101, 2905–2912. doi:10.1016/j.biortech.2009.11.102

USEPA, 2007. Concepts, Methods, and Data Sources for Cumulative Health Risk Assessment of Multiple Chemicals, Exposures and Effects: A Resource Document (Final Report). doi:EPA/600/R-06/013F

Wang, X., Deshusses, M.A., 2007. Biotreatment of groundwater contaminated with MTBE: Interaction of common environmental co-contaminants. Biodegradation 18, 37–50. doi:10.1007/s10532-005-9034-6

Wen, Q., Li, C., Cai, Z., Zhang, W., Gao, H., Chen, L., Zeng, G., Shu, X., Zhao, Y., 2011. Study on activated carbon derived from sewage sludge for adsorption of gaseous formaldehyde. Bioresour. Technol. 102, 942–947. doi:10.1016/j.biortech.2010.09.042

Wu, F.-C., Tseng, R.-L., Juang, R.-S., 2005. Preparation of highly microporous carbons from fir wood by KOH activation for adsorption of dyes and phenols from water. Sep. Purif. Technol. 47, 10–19. doi:10.1016/j.seppur.2005.03.013

Wu, T., Lin, Z., 2007. Electrochemical Behavior of Methyl Tert-Butyl Ether (MTBE) Oxidation on an Iridium dioxide (IrO2) Coated Electrode. J. Environ. Eng. Manag. 17, 49–56.

Wu, T.N., 2011. Electrochemical removal of MTBE from water using the iridium dioxide coated electrode. Sep. Purif. Technol. 79, 216–220. doi:10.1016/j.seppur.2011.02.008

Xu, X.-R., Zhao, Z.-Y., Li, X.-Y., Gu, J.-D., 2004. Chemical oxidative degradation of methyl tert-butyl ether in aqueous solution by Fenton's reagent. Chemosphere 55, 73–9. doi:10.1016/j.chemosphere.2003.11.017

Yang, S., Wang, P., Yang, X., Shan, L., Zhang, W., Shao, X., Niu, R., 2010. Degradation efficiencies of azo dye Acid Orange 7 by the interaction of heat, UV and anions with common oxidants: Persulfate, peroxymonosulfate and hydrogen peroxide. J. Hazard. Mater. 179, 552–558. doi:10.1016/j.jhazmat.2010.03.039

Yu, C., Fan, X., Yu, L., Bandosz, T.J., Zhao, Z., Qiu, J., 2013. Adsorptive Removal of Thiophenic Compounds from Oils by Activated Carbon Modi fi ed with Concentrated Nitric Acid.

Yu, L., Adams, C., Ludlow, D., 2005. Adsorption Isotherms for Methyl Tert -Butyl Ether and Other Fuel Oxygenates on Two Bituminous-Coal Activated Carbons. J. Environ. Eng. 131, 983–987. doi:10.1061/(ASCE)0733-9372(2005)131:6(983)

Yu, L., Zhong, Q., 2006. Preparation of adsorbents made from sewage sludges for adsorption of organic materials from wastewater. J. Hazard. Mater. 137, 359–66. doi:10.1016/j.jhazmat.2006.02.007

Zabaniotou, A., Theofilou, C., 2008. Green energy at cement kiln in Cyprus—Use of sewage sludge as a conventional fuel substitute. Renew. Sustain. Energy Rev. 12, 531–541.

doi:10.1016/j.rser.2006.07.017

Zhang, X. J., Wang, Z. S., Gu, X. S., 1991. Simple combination of biodegradation and carbon adsorption-the mechanism of the biological activated carbon process. Water Res. 25, 165–172.

Zhang, F.-S., Nriagu, J.O., Itoh, H., 2005. Mercury removal from water using activated carbons derived from organic sewage sludge. Water Res. 39, 389–95. doi:10.1016/j.watres.2004.09.027

Zogorski, J.S., 2005. MTBE and Gasoline Hydrocarbons in Ground Water of the United States MTBE and Gasoline Hydrocarbons in Ground Water of the United States. doi:10.1111/j.1745-6584.2005.0113.x

Zou, J., Dai, Y., Wang, X., Ren, Z., Tian, C., Pan, K., Li, S., Abuobeidah, M., Fu, H., 2013. Structure and adsorption properties of sewage sludge-derived carbon with removal of inorganic impurities and high porosity. Bioresour. Technol. 142, 209–217. doi:10.1016/j.biortech.2013.04.064

Zwank, L., Schmidt, T.C., Haderlein, S.B., Berg, M., 2002. Simultaneous determination of fuel oxygenates and BTEX using direct aqueous injection gas chromatography mass spectrometry (DAI-GC/MS). Environ. Sci. Technol. 36, 2054–2059. doi:10.1021/es010270x

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